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Food Technology

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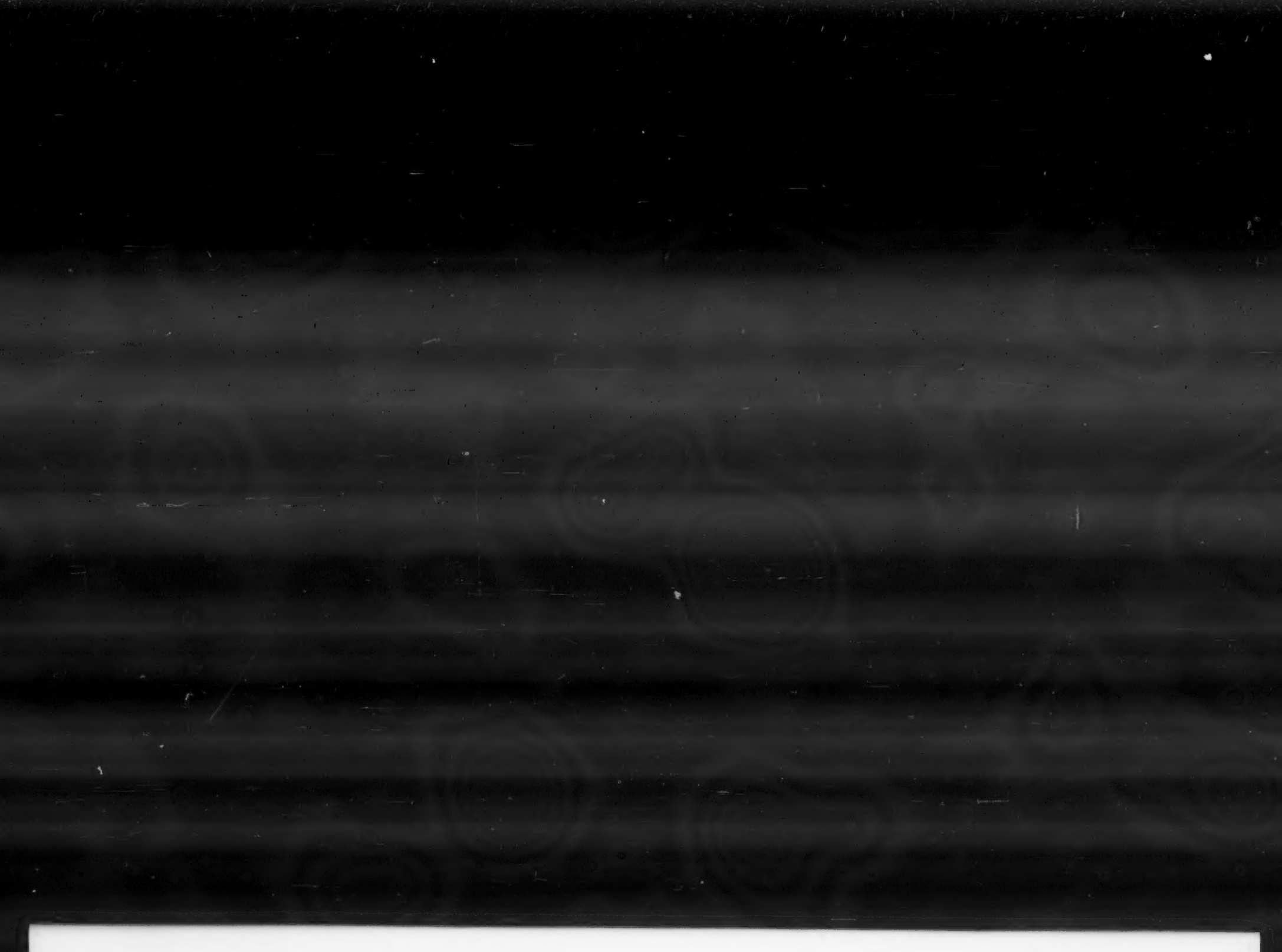

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Food Technology and Defense

The I. F. T. should never be forgetful of its responsibilities to the nation. Every war or possibility of future war brings new problems to those responsible for food supply for either offense or defense. All who are old enough to recall the situations which existed previous to each of the two World Wars can remember the confusion and the general interference, by presumably patriotic but often irresponsible purveyors of unproved products, with the hurried and not always clear-cut plans and methods of procedure which perhaps necessarily characterized the national unpreparedness that existed in each of these periods. In each, there was a question of obtaining sufficient quantities of food materials, and of assurance of technological and nutritional fitness for the special needs and ability to meet the requirements of the established military rations. A situation of this sort might happen again.

While this may be a condition that cannot be completely or possibly largely forestalled, the delay might be considerably minimized by planned cooperative assistance by competent scientific groups. None is as competent as the Institute of Food Technologists in clearly recognizing the great importance of food as a munition of war, both for offense and defense, and our organization might well organize its thinking and its objectives in such a way as to be of greatest and most immediate service in case the emergency should suddenly arise. Actual combat to protect one's home or land from attack is merely one simple form of defense. A larger and more important one is concerned with the provision of proper supplies for all divisions of the armed forces—the army, navy, air force, and the training camps, and for the associated ranks of the Red Cross, hospitals, and the thousands of non-combatants required in maintenance and in centers of supply on the home front. This might also include the feeding of workers in industrial plants commandeered for war work. Moreover, the same types of foods could meet the needs of much of our civilian population even in "the piping times of peace."

World War II taught us the necessity for prompt action. It also taught us that if we would avoid great waste, foods for defense must be nutritionally satisfactory both in quality and in acceptability. We learned also that they must be prepared not only against ordinary spoilage and deterioration but they must be able to withstand Arctic cold and Torrid heat without loss of value, and must be so packaged as to protect against moisture infiltration, insect and fungus attack, poison gas, rust or chemical deterioration, or the ravages of time. Much progress in most of these matters was attained during the latest war, but it was done the hard way and the costly way. Great service could be done for foods for general use by planned research along lines which were then begun.

There are probably innumerable "confidential" reports of value buried in official files. It seems that it might be wise to review and evaluate these, and to collect and collate the results of the experience of the past ten years, and see if some way to make new progress may not be derived from their study.

It seems not unrealistic to think that such a review, carefully studied and digested, might suggest some leads toward a more integrated relation between foods for defense and foods fully acceptable for commercial distribution and broad civilian consumption. After all, the consumers all have the same nutritive requirements, and approximately similar tastes. Moreover, the buying public is already familiar with many types of concentrated or condensed foods.

Here is also a posibility that might interest the broad-minded and far-seeing food manufacturer who appreciates what the trained food technologist might do for him by research, and by scientific methods of preparation, production, and control.

A survey of the troop-feeding programs in the United States Army from 1775 to 1940 showed the vast change in the ration in the long period up to and including the Civil War and the more humanized and nutritionally adequate ration of the World War II period which made the U. S. Army the best-fed group of our citizens. Principles and practices to be worked out by food technologists might bring defense foods and many special lines equally adaptable to adequate civilian consumption into the same general class. Then, at least, the soldier would not have the mistaken idea that he was receiving inferior food.

Individual members of I. F. T. are already cooperating officially with the Quartermaster Board, the Food and Container Institute, and other Federal agencies on matters bearing on problems of rations and control. Should not all members be able to use their professional equipment in intimate relation with the Army food problems either directly or through Selective Service channels?

In two wars we have seen the commercial rise and fall of dehydration as applied to fruits and vegetables and some other products, yet we fully know that this process of food preservation is rich in possibilities, and was of enormous value in the war. We have seen what were apparently properly prepared fruits and vegetables undergo changes in color and flavor by long storage under severe tropical conditions. We should be able to find a remedy by research. Other changes in well-prepared foods are known, especially in foods that we have used for defense and for supplying to less fortunate nations abroad. We are now investigating new methods of food preservation by high frequency and in other ways. In these we may find new procedures especially adapted to practical application in the quest for foods for defense, if unhappily, we are required to limit research in food production to this purpose. With the deep interest in food research and in new processes to broaden our food range on the home front, we should ever be on the alert to see wherein our new advances may find application also in the military or defense area.

The Committee recently established by the National Research Council undoubtedly has some of these broad objectives in view. Possibly a cooperating research committee from the I. F. T. could share in its work if coordinated assistance is sought.

Whether this be the case or not, we shall all join heartily in wishing it success in its efforts.

S. C. Prescott
President of I. F. T., 1939-1941

Editor's Note: The editorial on this page is the first in a series by past presidents of the Institute of Food Technologists, bearing on the relation of food technology to economic, health, and political problems of world-wide interest and importance. The second of the series will appear in the February issue.

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The Effect of Ultraviolet Light in the Meat Cooler on the Keeping Quality of Frozen Pork[a]

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When pork fat is exposed to ultraviolet radiation it is more susceptible to rancidity development during subsequent storage in the frozen state. Studies indicate that pork may have an appreciably shorter storage life at 0° or 10°F. when the meat cooler is equipped with ultraviolet ray lamps. The problem may be minimized by avoiding skinning the carcass or pork cuts prior to chilling or holding and by keeping the time between slaughter and freezing within 48 hours.

Introduction

The use of ultraviolet light in meat aging rooms has been widely accepted by the frozen food locker industry as a means of minimizing microbial growth and the development of off-odors. In beef aging rooms the use of ultraviolet light has made possible the maintenance of a higher room temperature to obtain a more rapid tenderization of the meat *(1, 4, 6)*. Freezer locker operators have been confronted with the problem of maintaining a sanitary plant, and of reducing contamination of the meat by microorganisms. The meat which is brought into the locker plant has been slaughtered and handled under a variety of conditions, which occasionally are very poor. Because of this situation many locker plant operators have installed ultraviolet lights in the meat aging rooms as a protective measure in reducing off odors and the development of slime and mold growth on the meat. A recent survey *(5)* indicates that 72 per cent of those frozen food locker plants in New York state having a meat cooler now are equipped with ultraviolet ray lamps.

Ozone is produced by the action of ultraviolet light on air. Whether the decrease in odors in aging rooms is the result of the ozone oxidizing the odorous gases or is due to a temporary blocking of the sense of smell is debatable. However, there is ample evidence that microbial growth can be significantly reduced by proper use of these lamps *(2, 3)*.

Both ultraviolet light and ozone are known to accelerate fat rancidity. This study was designed to determine to what extent UV lamps may affect the keeping quality, during prolonged frozen storage, of various meat products exposed to UV and ozone in the locker plant cooler.

Experimental

The keeping quality of meat may in part be expressed in terms of its tendency toward fat rancidification. The peroxide content of the fat before and during storage was used as a quantitative measure of the oxidation of fat in the meat. The fat was prepared for analysis by a cold extraction in low-boiling petroleum ether. The peroxide values (reported as m. eq. of peroxygen per kg. of fat) were determined by an iodometric procedure *(7)*.

A pilot study using beef, pork, and chicken was carried out to determine whether the use of ultraviolet lights in the cooler would shorten the life of these products in frozen storage. The beef loin was aged for ten days, the pork and poultry were held five days before packaging and storing at 0° F. The meat products indicated in Table 1 as "shaded UV treatment in cooler" were protected from the ultraviolet rays by means of a brown paper shield. The control samples were aged in a separate cooler not equipped with UV lights. The results of this exploratory study are summarized in Table 1.[c]

No detectable increase in peroxides in beef fat occurred during seven months' freezer storage even when ultraviolet ray lamps were operating in the cooler during the 10-day aging period. Chicken back fat did not become rancid after nine months' storage, whereas the fat taken from the abdomen, due to its exposure to air, had extremely high peroxide values after nine months. Again, the ozone or ultra-violet rays from the lamps had no effect on the storage life. The pork presented an entirely different picture in the exploratory study. The irradiated skinned pork loins showed a definite increase in peroxides during storage. The skin on the unskinned loin or shading the loin from the UV rays seemed to protect the fat against peroxide formation.

In this preliminary study, the samples were exposed to ultraviolet light in the meat cooler of a locker plant which had been using the lamps for some months, during which time the tubes had not been replaced or cleaned. Furthermore, only six lamps were installed in the rather large cooler. Accordingly, the UV irradiation was undoubtedly far below that recommended by manufacturers of the lamps.

In light of these results an experiment was planned wherein the studies on pork were expanded to give a more complete answer to the problem of chilling under ultraviolet light and the subsequent effects during storage.

Plan of experiment. The pork samples were subjected to the following conditions:

(a) One-half of the pork loins were skinned before being held in the cooler and the other half were held with the skin on to simulate the two procedures commonly employed in hog slaughtering and chilling.

[a] This study was supported in part by a grant by the Cooperative G. L. F. Exchange for meats research, a fellowship through the Philco Fund, and frozen food research grants by the Buffalo Niagara Electric Power Corporation; Carrier Corporation; Central Hudson Gas and Electric Corporation; Central New York Power Corporation; Consolidated Edison Company of New York, Inc.; Long Island Lighting Company; New York Power and Light Corporation; New York State Electric and Gas Corporation; Rochester Gas and Electric Corporation; and the Staten Island Edison Corporation.

[b] Philco Fellow.

[c] For many of the data in Table 1 we are indebted to Mr. L. H. Blakeslee, who initiated these early experiments.

TABLE 1

The effect of ultraviolet irradiation during aging on peroxide formation in beef, pork, and chicken fat during frozen storage

Product	Treatment in cooler	Initial	After treatment in cooler	(Months in storage at 0° F.)			
				4½	7	8	9
		1 [1] 2	1 2	1	1 2	1 2	2
				Peroxide Value [2]			
Beef	Control	2.0	1.9	....	0.4	....	....
	UV irradiated	2.1	1.6	....	0.6	....	....
	Shaded UV	2.1	5.0	....	0.7	....	....
Pork, skinned	Control	1.5-1.9	0.4-1.8	1.8	....	1.3-0.8	....
	UV irradiated	1.4-1.2	7.2-5.9	12.9	....	18.8-17.4	....
	Shaded UV	1.4-1.2	3.2-2.0	5.7	....	1.9-3.1	....
Pork, unskinned	Control	1.9-1.8	1.8-1.5	2.2	....	3.0	....
	UV irradiated	2.1-1.9	2.2-2.9	4.8	....	3.1-3.9	....
	Shaded UV	2.1-1.9	2.6-1.8	1.2	....	2.5-5.3	....
Chicken, back fat	Control	....	2.6-2.5	....	.... 4.0	....	7.7
	UV irradiated	....	1.4-3.2	....	.... 1.3	....	3.8
	Shaded UV	....	.... 1.9	....	.... 2.1	....	7.9
Chicken, abdomen fat	Control	1.8-2.5	2.7-1.7	....	.... 3.1	....	156.5
	UV irradiated	1.1-1.3	4.9-3.5	....	.... 5.7	....	176.8
	Shaded UV	0-1.1	1.5-2.4	....	.... 5.5	....	94.8

[1] The numbers 1 and 2 refer to two different samples. The peroxide values under heading 1 were all determined on the same sample. This is true also for the peroxide values listed under heading 2.

[2] Milliequivalents peroxygen/kg. of fat.

(b) The loins were held for two, four, or eight days in the meat cooler at approximately 36° F. and 90 per cent relative humidity. These prefreezing periods are not uncommon in locker plant practice.

(c) The upper sections of the loins were exposed to ultraviolet light (2537A) while the lower parts were shaded from the rays of the lamps to separately assess the effect of ozone generated by the lamps. Irradiation was provided by eight new Westinghouse Sterilamps, in a cooler 11 x 19 ft.[4] The intensity of UV output of the lamp nearest the meat (2 ft.) was 6.3 microwatts per sq. cm. per sec. at 38° F., the irradiation being measured at the source by means of a Rentschler "Click-Meter."

(d) All samples were frozen at 0° F. and stored at either 0° F. or 10° F.

Holding period. The pork carcasses with skin on were hung in the cooler for twenty-four hours after slaughter. The carcasses were removed from the cooler and the loins cut out. The loins were then hung at 36° F., either skinned or with the skin remaining intact. All control samples were obtained before the ultraviolet lights were turned on. The experimental samples were handled in this same manner, except that a shield of brown wrapping paper protected the bottom half of each loin from the UV light. This shield was constructed large enough to enable ample air circulation between it and the loin. The shield was allowed to hang approximately one inch below the loin to avoid interference from reflected ultraviolet light. Shielded samples were thus exposed to the ozone but not to the rays from the lamps.

At the end of the respective holding periods, the loins were removed from the cooler, the skin was removed from the previously unskinned loins, and the meat was cut into chops approximately one inch in thickness.

[4] We are indebted to the Empire Ultraviolet Equipment Co. for providing the Sterilamps.

Packaging, freezing, and storage. The individual chops were wrapped in one thickness of vaporproof Sylvania cellophane (P. M. F. B6 C. S., gauge 300) and then butcher-wrapped in a layer of medium weight brown wrapping paper. All samples were frozen for twenty-four hours at 0° F. After freezing, the samples were divided between storage compartments held at 0° and 10° F. Initial peroxide values were determined on all samples immediately after the freezing period. Storage samples were removed at appropriate intervals extending over a period of a year.

Sampling. The fat sample to be analyzed was obtained by cutting two thin strips of fat approximately 4 inches long and 1 mm. thick from the fatty edge of the chop, using a vegetable peeler. The use of this thin uniform outer strip of fat for analysis enabled an early detection of rancidity, since both the irradiation and the oxygen penetrate only a few millimeters. This method of sampling the fat is reproducible to within a few percent, and provides a 3-5 gram sample for analysis.

The fat was immediately extracted by grinding with purified sand and low-boiling petroleum ether. Anhydrous sodium sulfate was added during the grinding to remove the water present in the fat. This mixture was filtered into a 50 ml. volumetric flask and made to volume. The petroleum ether extracts could be held one or two days at 38° F. without causing any change in the peroxide value. The peroxide values were determined by the method referred to earlier *(7)*.

Results

The experimental data from this holding and storage study on pork samples are given in Tables 2, 3, and 4. The control samples, those held in the cooler without exposure to ultraviolet light or the traces of ozone produced, showed no significant formation of fat peroxides during one year's storage at 0° F. At 10° F. several of the samples were close to incipient rancidity (per. value = 15-20) at 44 weeks (Table 2).

The formation of peroxides in the experimental *unskinned* pork samples was similar to that in the control samples. The skin of the carcass protected the fat from any deleterious action of ozone, air, or of the ultraviolet light.

Removal of the skin before storing the meat in the freezer thus eliminated the exposed surface in which peroxide formation might have been accelerated. After 44 weeks' storage at 0° F. none of the samples showed incipient rancidity, and after 52 weeks only one had exceeded it (Table 3). Again, storage at 10° F. accelerated the formation of peroxides in the fat as indicated by elevated peroxide values at the 44- and 52-week sampling periods.

The formation of peroxides in the irradiated *skinned* pork samples was very rapid. The values for samples held four and eight days were approaching or had already passed the point of incipient rancidity when the initial analyses were made before placing the samples in freezer storage. On the other hand, the shaded skinned pork samples stored at 0° F. did not show an increase in peroxide value even after one year's storage (Table 4). Only one of three shaded skinned samples held at 10° for a year (that which had been held 8 days prior to freezing) had passed the point of incipient rancidity.

This apparent stability of the pork fat in samples exposed to conditions generally considered to be harmful (several days' delay in processing; storage at 10° rather than the recommended 0° F. or lower), was rather unexpected, as was the inconsistency of peroxide values of several other samples stored at 10° F. It was observed that at this storage temperature the pork fat developed rancid off odors and yet the peroxide values remained quite low (Tables 2, 3, 4). Several pork samples which had been stored at 10° F. and which showed unexpectedly low peroxide values were held for two weeks in the 0° F. freezer, then the peroxide values were repeated. In nine out of eleven such repeat analyses, the peroxide values at the end of the additional two-week period showed increases to levels ranging from 1.5 to 10 times the peroxide value at the end of the 10° F. storage period. This would indicate that the peroxides had been decomposing at a rate similar to the rate of formation when the pork fat was stored at 10° F. The peroxides, which are unstable intermediate products in fat rancidification, accumulated, rather than decomposing, when the pork samples were transferred to the 0° F. freezer. These observations suggest that the use of the peroxide determination as an objective, quantitative means of evaluating the progress of rancidity in frozen pork, while quite acceptable at a storage temperature of 0° F., may not be suitable at elevated storage temperatures.

Several practical implications are evident from the results of the present study. (a) A storage temperature

TABLE 2

The formation of peroxides in the control pork samples during frozen storage at 0 and 10° F.

Animal Number	Holding Period, Days	Condition of Carcass	Storage Temperature, ° F.	Storage period in weeks				
				Initial	8	16	44	52
				Peroxide value [1]				
1	2	Skinned	0	0	2.3	1.3	0.9	2.1
2	4	Skinned	0	0	1.2	0.2	0.8	2.1
3	8	Skinned	0	0	0.8	0.7	0.6	2.8
7	2	Unskinned	0	0	1.8	1.3	0	2.6
8	4	Unskinned	0	0	0.5	0	1.1	1.4
9	8	Unskinned	0	0	0.8	1.6	2.2	2.8
2	2	Skinned	10	0	0.7	0.7	13.8	10.2
3	4	Skinned	10	0	1.0	0.7	3.4	5.4
1	8	Skinned	10	0	2.0	0.8	2.1	2.9
8	2	Unskinned	10	0	0.7	0.4	16.0	43.0
9	4	Unskinned	10	0	1.1	0	2.5	3.9
7	8	Unskinned	10	0	1.7	1.7	10.1	40.2

[1] Milliequivalents peroxygen/kg. of fat.

TABLE 3

The formation of peroxides in the experimental unskinned pork samples during frozen storage at 0 and 10° F.

Animal Number	Holding Period, Days	Irradiated or Shaded	Storage Temperature, ° F.	Storage period in weeks							
				Initial	4	8	12	24	32	44	52
				Peroxide Value [1]							
10	2	Irradiated	0	3.1	0	0	1.3	0	....	0.6	0.7
11	4	Irradiated	0	0	0	1.2	1.6	1.4	....	2.2	5.9
12	8	Irradiated	0	1.9	1.9	2.2	0.8	1.3	....	1.2	4.4
10	2	Shaded	0	0	0	0	1.1	1.5	....	0.4	1.7
11	4	Shaded	0	0	0	0.9	2.6	0	....	5.7	6.8
12	8	Shaded	0	2.8	1.5	2.2	1.6	0	....	5.0	28.9
11	2	Irradiated	10	1.2	0.7	1.0	....	2.6	1.4	3.2	1.5
12	4	Irradiated	10	0	1.5	0.8	....	2.4	1.8	23.7	33.7
10	8	Irradiated	10	0	2.0	1.7	....	3.0	4.5	9.4	1.9
11	2	Shaded	10	0.6	0	0.9	....	1.6	1.7	10.5	18.3
12	4	Shaded	10	0	2.0	0.5	....	4.0	6.0	3.8	21.7
10	8	Shaded	10	0	2.0	2.1	....	2.6	2.0	2.0	2.3

[1] Milliequivalents peroxygen/kg. of fat.

TABLE 4

The formation of peroxides in the experimental skinned pork samples during frozen storage at 0 and 10° F.

Animal Number	Holding Period, Days	Irradiated or Shaded	Storage Temperature, ° F.	Storage period in weeks: Initial	4	8	12	20	24	32	44	52
				Peroxide Value [1]								
4	2	Irradiated	0	2.0	6.7	5.0	10.3	....	27.3	....	....	....
5	4	Irradiated	0	9.3	14.0	13.3	13.3	....	9.0	....	....	....
6	8	Irradiated	0	37.0	38.0	65.3	45.2	....	95.2	....	....	....
4	2	Shaded	0	0	0	0	1.4	0.5	....	....	....	....
5	4	Shaded	0	0	0.7	1.1	....	....	....	0.6	0.5	9.6
6	8	Shaded	0	1.3	2.2	2.8	....	3.0	....	2.2	1.1	3.0
5	2	Irradiated	10	6.5	9.0	8.9	9.6	7.1	5.3	....	....	....
6	4	Irradiated	10	18.4	22.4	27.8	32.1	....	48.3	....	....	....
4	8	Irradiated	10	23.1	30.4	51.5	38.7	....	81.3	....	....	....
5	2	Shaded	10	0	0	0.7	....	....	....	2.3	5.7	2.9
6	4	Shaded	10	1.0	1.9	2.3	....	1.1	....	2.2	2.8	2.5
4	8	Shaded	10	1.6	1.3	3.0	....	1.6	....	4.8	13.1	26.0

[1] Milliequivalents peroxygen/kg. of fat.

of 10° F. is too high for prolonged storage of frozen pork. (b) If ultraviolet lights are to be used in the meat cooler, the practice of leaving the skin on hog carcasses until immediately prior to processing is strongly to be recommended. (c) The small amount of ozone generated by ultraviolet lamps at 2537A has a negligible effect on the stability of the fat. This confirms the observations of Fredholm *(3)*. (d) A few days' delay in processing pork hung in coolers equipped with ultraviolet lamps may greatly shorten the storage life of the frozen product.

Summary

Ultraviolet irradiation of skinned pork carcasses during the period prior to freezing proved undesirable if the holding period exceeded two days. The fat of such meat turned rancid much more rapidly during subsequent freezer storage.

Shading the pork carcasses from the ultraviolet irradiation prevented the rapid formation of peroxides in the surface layers of fat, indicating that ozone played no important role in the rancidification catalyzed by the ultraviolet ray lamps.

Holding the carcasses with the skin on, and then removing the skin before storage, protected the pork fat against the deleterious action of the ultraviolet light.

Storage of pork at 10° F. accelerated the formation of peroxides in the pork fat and also the development of rancid odors. This elevated storage temperature particularly affected the stability of the irradiated pork samples.

Inconsistencies in the trend of peroxide values of pork fat stored at 10° F. emphasized the need for a method of evaluating the end products of fat oxidation rather than the determination of the unstable intermediate peroxides.

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NOTICE TO AFFILIATE MEMBERS

If you have the qualifications for full membership in the Institute a change of status to full Member is easily accomplished as follows:

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   The minimum training which shall qualify a candidate for eligibility for membership as a Member is, in general, graduation from a college, university, or similar institution in which he has majored in one or more of the sciences or branches of engineering associated with food technology. The minimum experience which shall qualify a candidate for eligibility for membership as a Member shall be three years in food technology. Any person who lacks the prescribed professional training but who, in the opinion of the Council, through long experience, has distinguished himself in food technology shall also be eligible for membership as a Member.

2. Write to the National Secretary or to the Secretary of your Regional Section for a "Change of Status" application form.

3. Fill this out with the exception of the signatures of three sponsors, and proceed according to the instructions for handling an application for membership on page 89 of the April 1948 issue of Food Technology.

Use of Liquid Sugars in Freezing of Apricots, Peaches and Nectarines[a]

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Data are presented to show the effect of various sugars on quality of frozen apricots, peaches, and nectarines. Sugar absorption, rate of auto-oxidation of ascorbic acid and rate of hydrolytic transformation of dehydro-ascorbic acid are shown as some of the basic data required to evaluate the protective effect of sugar for fruit.

Although a considerable amount of data on the most suitable procedures for freezing fruits in sirup to obtain maximum retention of color and flavor has been accumulated since the introduction of the use of sirup for frozen fruits in 1920 *(3)*, most of this data is based largely on subjective examination of experimental packs. There is relatively little technological data on the basis of which proper selection of sugar for use in freezing of fruit products could be made, and only rarely have experimental packs been made under commercial conditions from the packing lines *(5)*. In the evaluation of the most desirable types of sugars and densities of sirups to be used in the preparation of fruit for freezing storage, and of the best methods of using these sirups, it is necessary to know the ease with which they spread over fruit tissues, are held or are absorbed by them; their effect on rate of cooling, ice formation, and separation of unattractive sugar eutectics; their effect in preventing or minimizing changes in color brought about either by changes in natural pigments or discoloration by enzymic or non-enzymic oxidative processes; their effect on flavor, both as regards compatability with natural fruit flavors and their ability to promote the retention of the original flavors; and their effect on texture particularly from the colloidal point of view *(5)*.

To obtain technological data of this type, an extensive investigation of the freezing of apricots, peaches and nectarines was begun in our laboratories in the summer of 1946. Experimental packs were made to study the effect of various methods of applying sirup; to compare sucrose-sirups with those containing 30, 50, 70 and 90 percent invert sirup, and with those prepared from corn sugar, low conversion and high conversion corn sirup; and to compare the effectiveness of several anti-oxidants both with and without added citric acid. Fruit from the same source was used in all lots of sixteen packages each, and it was packed under commercial conditions in heat-sealed cellophane bags in top-opening Menasha cartons, overwrapped with waxed paper, frozen in a 14-stage Finnegan cross draft freezer, and stored at 0° F. Fifty-two lots of firm-ripe Blenheim apricot samples were packed on July 24 and 25, 1946, and graded November 13-17, 1946, April 2-7, 1947, and September 8-11, 1947. Forty-nine lots of Rio-Oso-Gem peaches were packed on August 14, 1946, and graded as above; nineteen lots of Kim and twenty-eight lots of Gower were packed on July 24 and 25, 1946, and graded the above dates. The samples were graded by about six tasters for color, flavor, texture and odor immediately after defrosting. In addition the drained weight of fruit, weight and density of cut-out sirup, color (by comparison with color charts and by photo-electric-colorimetry of alcoholic extracts), tannin content, ascorbic acid content, sugar content, acidity and pH of drained fruit and cut-out sirup were determined.

The solubility of oxygen in solutions of various sugars, and the effect of various sugars on the rate of oxidation of ascorbic acid, and on the rate of transformation of the primary product of oxidation, dehydro-ascorbic acid into 2, 3 keto gulonic acid, was measured.

This report will be limited to the presentation of data on the comparison of invert sirups with sucrose sirups, because of the present trend in the industry toward labor saving by the bulk handling of sugar. The distribution of solutions of sucrose, and of partially or almost completely inverted sucrose solutions, has been of great value to large users of sugar in reducing handling and storage costs and in facilitating preparation of sirups for use in various products *(4, 18)*. Although the more common physical properties of solutions of sucrose and of mixtures of sucrose and invert sugar have been summarized *(10)*, the possibilities and limitations of their use in the freezing of fruit products were not determined previously. Our data on this point are presented here together with preliminary data on sugar absorption, oxygen solubility and ascorbic acid transformation.

Acceptability of Invert Sirup in Frozen Fruit

Firm, ripe Blenheim apricots grown in Hollister, washed, halved and pitted, were taken from the packing line after sorting. Ten ounces of the fruit were placed in a cellophane bag in a one-pound top-opening Menasha carton, covered with 200 ml. of a 40° Brix sirup containing varying amounts of invert sirup, sealed, overwrapped, and frozen in 4 to 7 hours in a 14-stage Finnegan freezer at an air temperature of about —40° F. They were then stored at 0° F. until tested. Firm, ripe Rio Oso Gem peaches from Hollister, washed, steam-peeled, and sliced, were packed in similar cartons at the rate of 11 ounces of fruit to 5 ounces of 40° Brix sirup. Kim nectarines, a highly colored, yellow-fleshed, freestone nectarine, and Gower nectarines, a highly colored, white-fleshed, freestone nectarine, were washed, halved, pitted and packed at the rate of 10 ounces of fruit to 8 ounces of 40° Brix sirup in similar cartons, frozen and stored at 0° F. The nectarines were sorted for maturity so that the samples packed were from lots of fairly uniform quality, but the apricots and peaches were taken from the packing lines so that there was the same degree of variation in maturity that occurred in commercial samples. The analysis of composite samples

[a] Presented before the Eighth Annual I. F. T. Convention, Philadelphia, Pa., June 9, 1948.

of fresh fruit and of fruit preserved by dropping quartered or sliced fruit into hot 95 percent alcohol and heating for 30 minutes to inactivate invertase and other enzymes is shown in Table 1.

TABLE 1

Analysis of Composite Samples, Fresh and Preserved in Alcohol

	Apricots	Peaches	Kim Nectarines	Gower Nectarines
Preserved Samples				
Total solids	16.25	12.37	16.72	20.41
Alcohol soluble solids	14.00	10.67	12.60	17.73
Water insoluble solids	1.45	1.16	1.41	1.82
Acidity as citric	1.09	0.75	.....	0.90
Sucrose	6.69	4.06	6.66	8.23
Reducing sugars as glucose	2.75	3.37	2.40	3.05
Tannins	0.049	0.114	0.056	0.068
Fresh Samples				
Acidity	0.91-1.18	0.81	0.76	0.72
pH	3.75-4.0	3.67	3.80	4.13
Total soluble solids	14.50	11.70	17.10	20.10

Samples of the frozen apricots were removed from storage after about 3½ months, 8 months, and 12½ months; and 3, 8, and 13 months for peaches and nectarines. These were allowed to defrost at room temperature for about 5-6 hours while standing on edge in the carton, then opened and spread out on cut-out trays. The samples were observed for color immediately after all the ice had melted, and were tasted for flavor and texture while still cool (about 50° F.). The tastings were made on groups of twelve to fifteen samples, since we were interested in detecting readily noticeable differences in color, flavor and texture, rather than in discerning small differences. At each tasting, one lot was graded by all the tasters together and then used for comparison with the others. In judging the samples a numerical score was used: 1—Poor, 2—Fair, 3—Good, 4—Very Good, 5—Excellent. The taste panel was composed of from six to eight judges, three or more from our laboratory, and three from the C and H Sugar Refinery. Only two of the tasters were experienced judges of frozen fruits. The average scores obtained are shown in Tables 2 to 4.

TABLE 2

Subjective Scores for Apricots in 40° Bal. Sucrose and Invert Sirups

Code	%	Color			Flavor			Texture		
	Invert	I	II	III	I	II	III	I	II	III
AIA	0	2.7	2.4	2.5	2.9	2.9	2.0	3.0	2.9	2.0
AIIA-1	30	1.9	2.4	1.6	2.6	2.6	1.4	3.4	2.7	1.9
AIIA-2	50	2.6	2.8	1.6	2.8	3.0	1.5	3.2	2.6	1.8
AIIA-3	70	2.3	2.8	1.6	2.6	2.7	1.6	2.2	2.8	1.8
AIIA-4	90	2.6	2.7	1.8	2.6	2.5	1.8	3.3	2.9	1.8
AIIIA-3	0	2.5	2.9	2.3	3.0	2.7	2.7	3.0	2.7	2.7
AIIIA-9	90	2.9	2.2	2.0	3.0	2.7	2.0	2.8	2.6	2.8

TABLE 3

Subjective Grades for Peaches in 40° Bal. Sucrose and Invert Sirups

Code	%	Color			Flavor			Texture		
	Invert	I	II	III	I	II	III	I	II	III
P-3	0	3.0	2.1	2.2	3.0	2.3	2.0	3.5	2.5	3.0
P-6	30	2.6	2.1	1.8	2.9	2.9	2.6	3.4	2.8	2.7
P-7	50	3.1	2.1	2.3	2.9	2.4	2.4	3.3	2.6	2.8
P-8	70	3.1	1.6	1.9	2.7	2.6	1.5	3.3	2.5	2.5
P-9	90	2.6	1.8	1.8	2.6	2.4	1.4	2.9	2.8	2.9
P-35	0	2.7	2.1	1.9	3.2	2.1	1.4	3.0	2.7	2.4
P-45	0	2.6	2.0	2.0	3.1	2.3	2.1	3.5	2.4	2.5
P-41	90	2.5	1.8	2.0	2.8	1.7	1.3	3.1	2.3	2.0

TABLE 4

Subjective Grades for Nectarines in 40° Bal. Sucrose and Invert Sirups

Code	%	Color			Flavor			Texture		
	Invert	I	II	III	I	II	III	I	II	III
NK-2	0	3.4	3.4	3.0	2.9	2.9	3.0	3.0	3.3	3.0
NK-3	30	2.9	3.4	2.9	2.9	3.2	2.8	2.9	3.2	2.6
NK-4	50	3.1	3.6	2.9	3.2	3.2	2.8	2.9	2.9	2.9
NK-5	70	3.2	3.4	2.7	2.4	2.9	2.8	3.2	3.4	2.7
NK-6	90	2.7	3.1	2.6	3.0	3.0	2.7	3.0	3.2	2.8
NG-2	0	2.7	3.0	3.0	3.0	3.0	2.9	3.2	3.0	2.4
NG-10	90	2.9	2.6	3.0	3.4	2.8	3.0	3.4	2.8	3.0

The average scores for apricots indicate relatively little difference in appearance between apricots frozen in sucrose sirups and those frozen in invert sirups at the first and second tasting, but a definite decrease in score due to progressive discoloration in all invert sirups was apparent at the last tasting. There was no definite trend in texture, probably owing to variability of samples, except a marked increase in relative toughening of the skin with increase in storage period. This is reflected in a decrease of from 1 to 1.5 points in score, and this decrease was more noticeable in the samples packed in invert sirups. In flavor, at the first tasting, there was a noticeable difference between the 70 percent invert sirups and those of lower degree of inversion. This difference persisted in subsequent tasting. There was a noticeable decrease in flavor retention with storage time, the decrease being greater in apricots packed in invert sirups than those packed in sucrose sirups. The more discerning tasters detected an appreciable off-flavor at 70 percent inversion and a marked off-flavor at 90 percent.

In peaches there was little readily detectable difference in color between fruit frozen in sucrose sirups and those frozen in invert sirups at the first tasting, except at 90 percent inversion. The color score decreased with increase in storage time, the decrease being most noticeable at 8 months, but it was similar in sucrose and invert sirups. There was a noticeable decrease in texture at 90 percent inversion, but the trend was not definite owing to variations within the samples. As in the case with apricots, the texture of the samples was appreciably poorer with increase in storage time. There was an appreciable change in flavor at 70 percent inversion and a noticeable one at 90 percent which was more marked to the more discerning tasters. The flavor of the peaches decreased with increase in storage time, and this decrease was greater in the peaches frozen in 70 percent and 90 percent invert sirup. It was particularly noticeable as a combination of oxidized and foreign flavor, to the discerning tasters.

In Kim nectarines there was an appreciable discoloration at 90 percent inversion which persisted throughout the storage period. Kim nectarines retained their color better, however, than did apricots or peaches. In texture there was little difference between the sucrose and invert sirup samples. Unlike apricots, the nectarine skin was thinner and tender, and remained so during storage. In flavor there was a slight difference at first in invert sirup, noticeable at 70 percent inversion, but this difference did not persist, owing largely to variability of samples. In general, nectarines were of higher flavor initially, and retained their color and flavor better

TABLE 5

Distribution of Soluble Solids After 6-8 Months Storage at 0° C.

Code	Ingoing Weights Grams		Drained Weights Grams		Soluble Solids %		pH		Acidity % as citric	
	Fruit	Sirup	Fruit	Sirup	Fruit	Sirup	Fruit	Sirup	Fruit	Sirup
AIA	280	235	201	242	17.9	35.6	3.85	3.91	0.69	0.32
AIIA-1	280	235	282	238	17.8	34.0	3.80	3.87	0.60	0.39
AIIA-2	280	235	251	244	18.4	32.4	3.80	3.85	0.53	0.46
AIIA-3	280	235	252	248	18.9	30.1	3.75	3.80	0.65	0.46
AIIA-4	280	235	258	248	19.9	31.6	3.80	3.80	0.63	0.44
AIIIA-3	280	235	282	218	17.1	37.0	3.34	3.49	0.70	0.32
AIIIA-4	280	235	273	242	17.1	43.1	3.22	3.34	0.70	0.40
P-3	312	142	294	149	19.0	21.9	3.70	3.67	0.53	0.47
P-6	312	142	289	152	19.0	23.0	3.69	3.72	0.50	0.55
P-7	312	142	296	145	19.0	24.0	3.69	3.70	.....	0.44
P-8	312	142	274	163	21.4	21.0	3.79	3.90	0.46	0.47
P-9	312	142	272	145	19.8	21.0	3.71	3.85	0.53	0.51
P-35	312	142	315	123	17.5	23.7	3.68	3.72	0.49	0.49
P-45	312	142	295	140	18.0	25.4	3.62	3.64	0.46	0.47
P-41	312	142	289	108	19.2	23.2	3.61	3.71	0.51	0.46
NK-2	284	227	267	243	22.9	32.9	3.86	4.13	0.35	0.16
NK-3	284	227	271	234	21.7	32.7	3.84	4.20	0.50	0.20
NK-4	284	227	248	253	22.6	31.4	3.50	3.70	0.46	0.33
NK-5	284	227	268	228	21.9	32.9	3.79	4.00	0.58	0.24
NK-6	284	227	261	238	24.4	32.1	3.99	4.17	0.44	0.23
NG-2	284	227	261	240	23.5	34.2	3.75	3.90	0.62	0.27
NG-10	284	227	255	161	25.4	29.3	3.92	4.02	0.50	0.37

during freezing storage than did the apricots or peaches. In Gower nectarines there was no appreciable difference in color, flavor, or texture between sucrose and 90 percent invert sirup samples. The more careful tasters reported less difference between nectarines frozen in sucrose and in invert sirups than was found for apricots and peaches.

The analytical data obtained on these samples are summarized in Tables 5 to 7. Since these data were obtained by several individuals whose laboratory technique differed, they are subject to variable analytical errors, and in addition are subject to sampling errors caused by the purposely uncontrolled variation in composition with the normal variation in maturity occurring under commercial processing conditions. Again our attention was focused on significantly large changes and trends, rather than on small differences.

The data summarized in Table 5 indicate no significant trend in drained weight with degree of inversion of sirup and little change in soluble solids, pH, or acidity. In comparison with similar determinations on fresh fruits, the soluble solids content of frozen apricots increased by about 4 percent, the pH of the fruit increased, and the acidity decreased, largely due to movement of acids out of the fruit tissue into the sirup. These changes occurred largely during defrosting. The soluble solids content of peaches increased by about 6 percent, and of nectarines by about 4 percent. The peaches remained at about the same pH value after freezing and freezing storage and defrosting, but their acidity decreased. The pH values of Kim nectarines were essentially the same in fresh and frozen fruit, but those of Gower nectarines decreased slightly. The acidity in fruit tissues decreased apparently, owing to leaching.

The data in Table 6 show a comparison between the color rating and actual color as shown by comparison with Maerz and Paul color charts *(12)*. There was no significant change in tannin content of the frozen apricots and nectarines, but a definite decrease in that of peaches, partly due to leaching and partly to oxidation. There was an appreciable increase in sugar content, but very little significant change in sucrose content of the samples packed in sucrose and invert sirup. The available data were too erratic for definite conclusions other than that the natural sucrose content was not appreciably altered by invertase activity.

The degree of retention of the naturally present ascorbic acid content of the fruit samples is shown in Table 7 after 4-5 months and 11-12 months of storage. The original ascorbic acid content of the fresh fruit was not determined. The more commonly accepted values for the ascorbic acid content of apricots vary from 4-10 mg. per 100 gm. and of nectarines 8-25 per 100 gms. The values we found for samples prepared under conditions such as to eliminate enzymic oxidation are in the same range, about 8 mg. for apricots and peaches and about 20 mg. for nectarines. In general the data indicate that the ascorbic acid retention in apricots and peaches was much poorer than in nectarines, particularly the Gower

TABLE 6

Color Rating, Tannin and Sugar Content

Code	Color Rating	M & P Color	Tannin Content		Sugars		
			Fruit	Sirup	Soluble Solids as Sugars	Sucrose	Total
AIA	2.4	P10J10	0.011	0.019	17.9	11.1	14.5
AIIA-1	2.4	P11J11	0.065	0.025	17.8	9.3	14.7
AIIA-2	2.8	P11K9	0.077	0.029	18.4	6.2	12.8
AIIA-3	2.8	P10L9	0.020	0.062	18.9	6.3	14.5
AIIA-4	2.7	P11K9	0.005	0.038	19.9	5.1	14.5
AIIIA-3	2.9	P10I9	0.049	0.048	17.1	7.6	10.9
AIIIA-4	2.5	P11K10	0.049	0.055	17.1	9.1	12.2
P-3	2.1	P11K7	0.084	0.046	18.1	11.2	15.5
P-6	2.1	P11K7	0.049	0.042	19.1	6.7	14.1
P-7	2.1	P11K7	0.029	0.029	.....	.....	.....
P-8	1.6	P12K8	0.029	0.000	21.4	.....	14.4
P-9	1.8	P13J8	0.031	0.017	.....	.....	.....
P-35	1.9	P11L8	0.054	0.023	17.5	8.1	10.8
P-45	2.0	P11L8	0.071	0.013	.....	.....	.....
P-41	2.0	P11K8	0.041	0.035	19.2	4.1	16.4
NK-2	3.4	P11L10	0.033	.....	22.9	.....	.....
NK-3	3.4	P11L9	.....	.....	21.7	5.0	9.4
NK-4	3.6	P11K10	.....	.....	22.6	14.6	19.5
NK-5	3.4	P10J8	.....	.....	.....	.....	.....
NK-6	3.1	P11K9	.....	.....	.....	.....	.....
NG-2	3.0	P5H7	0.052	0.013	23.5	16.0	18.7
NG-10	3.0	P6F10	0.065	0.000	.....	.....	.....

TABLE 7

Ascorbic Acid Content in Mg. per 100 grams

Code	After 4-5 months				After 11-12 months			
	Drained Weight		Ascorbic Acid		Drained Weight		Ascorbic Acid	
	Fruit	Sirup	Fruit	Sirup	Fruit	Sirup	Fruit	Sirup
AIA	256	214	0.9	0.7	245	228	4.0	0.0
AIIA-1	267	195	1.5	0.0	248	230	3.2	0.22
AIIA-2	271	217	0.0	0.0	256	238	0.45	0.21
AIIA-3	273	210	0.0	0.0	259	195	0.58	0.65
AIIA-4	270	224	0.0	0.0	255	235	0.0	0.0
AIIIA-3	270	217	0.1	0.2	259	207	0.0	1.05
AIIIA-4	265	137	2.6	0.7	256	154	1.2	0.26
P-3	329	71	1.5	1.0	302	106	0.93	0.0
P-6	299	103	1.6	0.5	314	90	0.32	0.0
P-7	305	103	1.4	0.6	293	113	0.51	1.9
P-8	306	111	1.7	0.4	317	91	0.47	0.0
P-9	301	121	0.9	0.3	306	102	0.33	0.0
P-35	299	124	1.3	0.0	288	127	0.70	0.2
P-45	293	121	0.8	0.0	283	126	0.31	0.12
P-41	303	123	0.4	0.0	293	114	0.17	0.0
NK-2	225	226	0.0	2.0	249	191	9.0	2.2
NK-3	256	230	0.0	2.6	246	222	9.4	2.6
NK-4	276	201	9.0	2.3	279	198	7.9	2.7
NK-5	271	214	6.7	1.7	260	215	8.0	2.0
NK-6	268	214	8.4	2.0	268	204	5.7	1.1
NG-2	288	143	17.4	6.5	279	192	23.6	8.7
NG-10	275	196	10.6	5.5	252	150	20.4	9.2

variety. There is some indication that in apricots ascorbic acid retention was progressively poorer in sirups of increasing degree of inversion. This trend was not observed in peaches, and Gower nectarines, but did occur in Kim nectarines. Other observations indicated that the phenolase oxidation of ascorbic acid was inhibited more by sucrose than invert sirup, but these investigations are still in progress. The ascorbic acid losses were greatest in the initial storage and did not increase with length of storage period; if at all, the recovery was better from samples frozen for one year than those frozen for four months. The sirups drained from the fruit contained little ascorbic acid except in the case of nectarines. In Kim nectarines ascorbic acid retention was much better in sirups containing 70 percent or less of invert sugar than in the 90 percent invert sirups.

Absorption of Sugar by Frozen Fruit

The absorption of sugar by fruit frozen with added sugar or sirup has long been considered desirable to improve preservation of color and flavor and to yield a better tasting product. To obtain better sirup penetration in berries, Wiegand *(20)* suggested cold storage of the packaged fruit and sirup at 30-31° F. for 24 to 72 hours, and this was confirmed by extended tests in our laboratories *(7)*. The total quantity of sugar absorbed by the fruit, however, is small in comparison with change in weight caused by withdrawal of water as shown in Table 8. In addition to delayed freezing, impregnation deaeration was investigated in our laboratories. Most of the sugar exchange occurred during defrosting rather than freezing storage in our studies which will be reported in more detail elsewhere.

Effect of Sugars on Oxygen Solubility

Since oxidation during freezing, freezing storage, and defrosting is detrimental to color and flavor retention, it is desirable to reduce this to a minimum at all stages of processing and distribution. The rate of this oxidation is determined by the amount of oxygen present in fruit tissues, the amount of oxygen present in the sirup added to the fruit, and the amount of oxygen diffusing from the surrounding air into the package. It has been commonly observed that in preparing sirups by dissolving granulated sugar in water at room temperature considerable quantities of oxygen are dissolved in the sirup. Repeated tests have shown large amounts of oxygen in cold sirups as used in plants. To obtain data on the solubility of oxygen in sugar solutions and the effect of concentration and method of production on oxygen content, the oxygen content of a number of sirups under various conditions was obtained by a modified polarographic method *(11)*. These data *(9)* were briefly summarized at the Annual Meeting of the Northern California Section of the Institute of Food Technologists on December 4, 1947, and are presented in part here. As the data in Table 9 indicate there is a marked reduction in solubility in sugar sirups in comparison with water, the solubility of oxygen being least in a 90 percent inverted sirup, and less in corn sirups than in sucrose solutions.

TABLE 9

Oxygen Solubility of Various Sugar Sirups at 40° Bal. and 22° C.

Sugar	Oxygen Solubility in ml. per 100 ml. of sirup
Control	0.636
Cane sugar	0.256
Corn sugar	0.238
Levulose	0.227
Dextrose	0.218
High conversion corn sirup A	0.204
High conversion corn sirup B	0.204
Invert sirup (0-90)	0.105

TABLE 8

Water Lost and Sugar Absorbed in 50° Bal. Sirup Packs

Fruit	Treatment	Water Lost %	Sugar Absorbed %	Authority
Strawberries	whole	39.35	2.75	Wiegand (21)
Strawberries	whole, frozen at once	42.5	3.2	Joslyn & Marsh (7)
Strawberries	whole, stored for 24 hrs. at 32° F.	40.0	6.7	Joslyn & Marsh (7)
Strawberries	whole, frozen at once	28.4	3.7	Joslyn & Marsh (7)
Youngberries	whole	22.6	0.0	Marsh (13)
Red raspberries	whole	22.2	5.25	Wiegand (21)
Boysenberries	whole	13.70	0.30	Wiegand (21)
Apricots	halved	5.35	3.19	Wiegand (21)
Apricots	sliced, frozen at once	24.2	5.1	Marsh (13)
Apricots	sliced, stored at 32° F. for 24 hrs.	29.0	4.0	Marsh (13)
Apricots	sliced, stored at 32° F. for 48 hrs.	30.2	3.1	Marsh (13)
Apricots	sliced, stored at 32° F. for 72 hrs.	30.8	5.6	Marsh (13)
Peaches	sliced	30.80	1.75	Wiegand (21)

The effect of method of preparing sirups is shown in Table 10. In one case the sirups were prepared by dissolving the necessary amount of granulated sugar in water at 20° C. with vigorous stirring; in the other case the water was brought to boiling and the sugar dissolved with minimum of stirring and then allowed to cool to 20° C. in uncovered beakers. There was little difference under these conditions at lower densities, but the percentage difference progressively increased with increase in density. Some diffusion of oxygen undoubtedly occurred during cooling of the hot sirup, but this would also occur under commercial practice. These data indicate but little difference between the two methods. Under commercial practice, however, occluded oxygen as well as dissolved oxygen would be incorporated in the sirup.

TABLE 10

Effect of Method of Dissolving Granulated Cane Sugar on Oxygen Content

	Sirup density, ° Bal.			
	20	30	40	50
Solution in cold with stirring	0.315	0.227	0.168	0.108
Solution in hot	0.305	0.219	0.142	0.078

Relative Effect of Sugars on the Rate of Auto-Oxidation of Ascorbic Acid

It has been demonstrated in our laboratory and elsewhere that darkening and discoloration of fruit tissue injured by freezing, mechanical injury, or by suboxidation will not occur until the residual ascorbic acid content is reduced below the level at which it will maintain the chromogens (phenolic derivatives) in the reduced stage. Thus it is important to conserve both the naturally occurring ascorbic acid and that added in processing. Oxidation of ascorbic acid, by both enzymic and non-enzymic processes, is inhibited to varying degrees by sugars, and we have found that sugars may exert a specific effect in both instances. Investigations on the extent and mechanism of this effect have been under way in our laboratory for the past two years as well as earlier *(7)*. That sugars do exercise a protective effect on non-enzymic oxidation of ascorbic acid has been established by others *(2, 14, 17, 19)*, but there is a considerable confusion in the literature on the relative effectiveness of the sugars.

Richardson and Mayfield *(17)* reported that sucrose and white corn sirup exerted a protective influence on ascorbic acid oxidation while dextrose showed a tendency toward destructive influence during boiling. Munilla and Vogelsinger *(14)* reported that addition of sugars reduced the rate of oxidation of ascorbic acid solutions stored at 20° C., lactose having least effect and dextrose and sucrose most. The Japanese investigations *(19)* reported that citric acid, fructose, and sucrose promoted oxidation while glucose inhibited it. Chamrai *(2)* established the protective effect of sucrose and pointed out that at low pH this was due to its effect on reducing rate of diffusion of oxygen into his solutions, and at higher pH values to its copper-binding power.

Our data indicate that this in part can be explained by differences in Cu and Fe content caused by the presence of variable amounts of these metals in the sugars used and by differences in oxygen tension. We have investigated the effectiveness of various sugars at various pH values and under two different experimental conditions on the auto-oxidation of ascorbic acid *(8)*.

TABLE 11

Effect of Sugars on Auto-Oxidation of Ascorbic Acid Solutions Allowed to Stand Exposed to Air at 22° C. in Presence of 40% Sugar or Sirup Solids

Sugar	Cu p.p.m.	Fe p.p.m.	Percent of ascorbic acid oxidized	
			24 hours	48 hours
None	.....	.....	57.2	83.5
Low conversion corn sirup	0.70	8.3	19.2	30.4
High conversion corn sirup B	1.13	28.1	10.0	14.7
High conversion corn sirup A	9.85	10.0	26.5	48.2
Dextrose	0.34	.....	12.4	42.5
Levulose	0.10	7.6	12.6	17.8
Lactose	0.70	14.4	17.3	30.1
Maltose	0.20	11.2	8.2	16.3
Sucrose	0.0	5.0	18.0	31.7
Sirup (type 0)	0.39	15.2	21.5	36.7
Sirup (type 0-90)	0.27	14.2	17.8	21.2

TABLE 12

Effect of Sugars on Auto-Oxidation of Ascorbic Acid Solutions at 30° C. With Oxygen Bubbled Through at Rate of 97 Ml. Per Min. at 40% Sugar or Sirup Solids

Sugar	% ascorbic acid oxidized in 2 hours
None	62.5
Low conversion corn sirup	49.6
High conversion corn sirup	
B	24.9
A	100.0
Dextrose	14.9
Levulose	32.2
Lactose	62.8
Maltose	12.6
Sucrose	24.7
Sirup, type 0	48.0
Sirup, type 0-90	49.6

Typical data are summarized in Tables 11 and 12. Of the pure sugars tested, the most efficient in retarding oxidation of ascorbic acid in solutions containing about 50 mg. percent of ascorbic acid allowed to stand quietly exposed to air at room temperature were maltose, levulose, and lactose; the least effective was dextrose. In the case of sirups, the most effective were high conversion corn sirup B and invert sirup; the least effective was high conversion corn sirup A. The sample of the latter which we tested also happened to contain the highest amount of copper. Under conditions of vigorous oxygenation, however, the order of decreasing protection was maltose, dextrose, sucrose, and lactose. The order of decreasing protection in sirups was: high conversion corn sirup B, sucrose, invert sirup, corn sirup (low conversion), and high conversion corn sirup A. In the first case oxygen solubility and rate of diffusion of oxygen were limiting factors which were not involved in the second case. These results are typical of the general trends observed in our investigation to be reported elsewhere.

Effect of Sugars on Rate of Transformation of Dehydro-Ascorbic Acid

In spite of the extensive investigations that have been reported on various aspects of Vitamin C retention in foods, we know very little about the mechanism of

ascorbic acid destruction in processed foods. As pointed out by Cameron *(1)*, until some fundamental work is applied to this problem we shall have to deal with the situation empirically. All that we know definitely is that ascorbic acid can be transformed reversibly by mild oxidation into dehydro-ascorbic acid which is still largely biologically active. Dehydro-ascorbic acid is postulated to exist either in the triketo form or in the hydrated form, but since it has not to date been obtained in pure crystalline form as a product of oxidation, our knowledge of even this reaction mechanism is not complete. The dehydro-ascorbic acid by irreversible hydrolysis of the lactone ring can be transformed into 2, 3 diketo gulonic acid, biologically inactive. The gulonic acid also has not been isolated in pure crystalline condition.

On subsequent oxidation it or dehydro-ascorbic acid is transformed into oxalic and threonic acids. Although several acceptable methods of analyis for ascorbic acid are available, satisfactory methods for the determination of dehydro-ascorbic acid and the other products, particularly as they occur in foods, are not known. Recently, however, Penney and Zilva *(15, 16)* have suggested and applied a method for the determination of gulonic acid in the oxidation products of ascorbic acid. We have applied their method to the investigation of the effect of sugars on the rate of conversion of dehydro-ascorbic acid into gulonic acid. Typical data are presented in Table 13 which shows the extent of conversion

TABLE 13

Effect of Sugars on Transformation of Dehydro-Ascorbic Acid into 2, 3 Diketo Gulonic Acid

Sugar or sirup	Concentration %	Percent Conversion	
		10 hours	20 hours
None	.....	34.5	53.0
Fructose	20.0	30.0	48.0
Dextrose	20.0	26.5	40.0
Lactose	20.0	19.0	37.5
None		35.5	53.0
Dextrose	40.0	21.5	32.5
Sucrose	40.0	33.5	47.0
Maltose	40.0	28.0	37.5
None	.....	35.0	53.0
High conversion corn sirup A	40.0	32.0	43.0
High conversion corn sirup B	40.0	25.0	35.0
Glucose	40.0	29.5	40.5

of a freshly prepared 0.1% dehydro-ascorbic acid solution into gulonic acid at 28° C. and pH 5 (McIlvain's buffer).

The data presented, which were previously reported at the December 4, 1947, meeting of the Northern California Section of the Institute of Food Technologists, indicate that sugars do decrease the rate of this conversion. At a concentration of 20 percent, lactose was most effective and levulose least. At a concentration of 40 percent, dextrose and high conversion corn sirup B were most effective, and sucrose least so, initially. Later the order of decreasing effectiveness was dextrose, high conversion corn sirup B, maltose, glucose sirup solids, high conversion corn sirup A, and sucrose. It is likely that the reported losses in Vitamin C content of foods heated in absence of oxygen may be due to reactions of this type, and there is some evidence that dehydro-ascorbic acid is more thermolabile and more reactive with amino acids than ascorbic acid. More work in this field is now under way in our laboratories.

Summary and Conclusions

There is relatively little available technological information on the basis of which proper selection of sugar for use in frozen fruit products could be made other than by empirical means subject to the human error of any particular taste panel appraisal.

On the basis of such taste panel appraisal, the color, flavor, and texture retention in frozen apricots and peaches were influenced by degree of inversion of sucrose. Nectarines were less sensitive to this effect. In general sugar sirups containing more than 50 percent invert sugar are not satisfactory liquid packing media for such fruits.

Data are presented to show that sugar absorption, oxygen solubility, rate of auto-oxidation of ascorbic acid, and rate of hydrolytic transformation of dehydro-ascorbic acid, are affected by the kind and concentration of sugar used. These are but some of the basic data required to evaluate the protective effect of sugar for a particular fruit product.

Acknowledgment

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Non-Alcoholic Beverages[a]

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A review of the whole field of non-alcoholic beverages is given. A brief history, covering the origin and development of the non-alcoholic beverages is included with the description of some of the products. Present trends in the non-alcoholic beverage industry are discussed.

The beverage industry is large, important, and is worthy of the attention of the Food Technologist. Many kinds of beverages have been devised, from time to time, in various parts of the world, yet in this country there has been so much standardization on a relatively few types that many of potential value may have been overlooked.

The American Bottlers of Carbonated Beverages is offering the Chesterman award of $1000 in cash for the most outstanding technical contribution made during each calendar year to the progress and advancement of the soft drink industry: an indication that the industry appreciates the need of research and development.

Beverages perform many services besides the obvious one of slaking thirst. Most drinks have important food value; it is hard to say, for instance, whether milk should be classed as food or beverage. Some have stimulating value and tend to keep one awake and lively because of a content of caffeine, whereas others are mildly sedative, favoring sleep. Herb teas and mineral waters sometimes have medicinal action, but today, in view of the multitude of medicines of high activity that are available, any slight medicinal function is largely ignored. In some places, however, certain drinks are still called "tonics." Perhaps the biggest argument for the use of beverages is that they constitute a treat or mild indulgence that can be enjoyed by the individual or that provides a ritual to go with sociability.

Water as a Beverage

Water is the oldest beverage and the most important. The fact that water from any source may be used for drinking purposes calls for practically every water supply being given sanitary and flavor consideration. Spring waters and deep wells may be depended upon to be clean and wholesome, but large stream or lake sources of adequate purity are becoming more and more difficult to find. As a consequence, treatment of water supplies has become standard practice nearly everywhere, often with adverse effect on the flavor. Algae growing in reservoirs in late summer, and most industrial wastes, injure flavor. As a consequence, flavor improvement of water, to make it fit and attractive to drink, has become a large and important business. The water from many city water systems, especially those along the Atlantic seaboard, is normally pleasant. In highly industrialized areas, the chlorinated organic taste often drives people to seek supplementary sources for drinking purposes and for the making of tea and coffee. Chemical and adsorbent treatments to eleminate bad tastes are being developed, however, as well as deionization and distillation, and it is expected that before long nearly every tap will yield pleasant-tasting water.

Water is generally preferred cool and many want it actually iced. No clean-cut information is available that harm comes from drinking ice water, at least when it is sipped. Physiologists point out, however, that when very warm or very cold drinks are taken with meals, they should be drunk slowly so as neither to overstimulate nor to impede digestive action. Physiologists seem not to be particularly concerned about dilution of the stomach contents by even large amounts of imbibed liquid. Generally, any advice given is in the direction of drinking more water than is usually taken.

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Carbonated Beverages

There seems little doubt that it was the English chemist Priestley who discovered that artificially carbonated water was safe to drink. He found that it had a taste similar to that of water from certain celebrated springs. The Swedish chemist Bergmann checked Priestley's findings a few years later, in 1770. It was in Philadelphia, however, whence Priestley fled, that carbonated water was first consumed in quantity, in 1785. There, a Dr. Philip Physick treated patients with carbonated water as a medicine. His pharmacist, Townsend Speakman, added fruit juices *(1)* to some of the carbonated water which then could be used as a beverage: the first "soda," "pop," or "tonic." This production of beverages in an apothecary shop led other pharmacists including Elias Durrand, also of Philadelphia, to produce a series of combinations of soda water with indigenous and exotic flavorings, and mixtures, leading to sarsaparilla, root beer, ginger ale, numerous specialty drinks and finally to the "cola" drinks. The end has not yet been reached, but the active development period seems to be over and new types have appeared less and less frequently during the past fifty years.

Up to the present, the only gas used for "charging" water appears to have been carbon dioxide.

Bottled carbonated waters are rarely drunk plain in this country, as is common in Europe, but are used chiefly as "mixers" for various drinks, both alcoholic and non-alcoholic. Some of these waters contain enough salts to produce a distinct "mineral" flavor, which "goes well" in mixtures.

It is common American practice to combine flavored, colored and acidulated sirups with carbonated water in automatic filling machines. A measured quantity of the sirup is first injected into the bottle, which is then filled with cold carbonated water. The residual air at the top may be replaced by carbon dioxide by a puff of the latter. The bottle is then capped, and mixing is accomplished by one or more inversions of the bottle. In this manner, gingerale, cola drinks and fruit flavored drinks are produced. A new item thus produced, is flavored with volatile apple concentrate, of the type invented by Howard Milleville *(2)*.

Some idea of the volume of sales of carbonated soft beverages may be gained from the quantity of sugar used, about half a million tons per year or about 3.4% of the total sugar used in this country. One manufacturer claims to supply over 100 drinks per year for every person in the land, a retail sales volume of well over half a billion dollars. There are about 6000 plants and warehouse points, virtually all of which are locally owned and operated, giving direct employment to 80,000 to 100,000 people and utilizing nearly 50,000 trucks for transportation.

The Caffein Beverages

Tea is a contender for first place as the most ancient extracted beverage *(3)*. It could have originated either in India or in China, for the shrub is indigenous to both countries. However, it has been referred to only in the Chinese literature, first about three thousand years ago. It did not reach Japan until the ninth century or Europe until the 16th.

Tea is best prepared by extraction of the leaves by very hot water. Any boiling after addition of the tea makes for bitterness and astringency, from the tannin, but strangely enough some people prefer boiled tea. Today, a large proportion of tea is sold in convenient bag form. The blend is usually adjusted for best flavor with the water available in the district in which it is distributed. The flavor of tea is much affected by the water from which it is made. Regardless of the kind of tea, whether it is the plain-dried green teas or the leaves that have been carefully fermented before drying to make black tea, it should be brewed in a pot. With pot-brewing, the water will be hotter than the critical 180° F. point, where the rolled leaves open up and good extraction ensues. The present restaurant habit of serving an uncovered cup of merely warm water for extracting the tea is doing this beverage much harm.

While tea has a pleasing though mild aroma, some producers intensify and sweeten the normal flavor by adding jasmine flowers or rose petals to cans of the dry tea. Sometimes the petals are left in the tea, but more frequently they are removed after most of their fragrance has been transferred to the tea. Even a second or third flower addition may be made to produce the highest flavor. There are localities where tea leaves are dried in an atmosphere of smoke, which imparts a mild creosoty character that some people like.

Maté or "Paraguay tea" is very popular in South America where it has been used for an indefinitely long time. The flavor is reminiscent of that of smoky Asiatic tea, but it is usually too smoky to appeal to most North Americans or Europeans. A North American beverage called "Cassina" or "Yaupon" is produced from a variety of the holly bush similar to that from which Maté is made. It has not become widely used in spite of at least one attempt at its popularization.

Coffee is another drink of considerable antiquity, going back certainly for five hundred years and likely for over a thousand years in Ethiopia and in Arabia where the wild tree is indigenous. Tradition implies that it has been used in these countries since time immemorial. The first "coffee house" appeared in England in 1650 as a sort of club or social center. It is probable that both Greeks and Turks appreciated coffee, as they still do, considerably earlier than did the English, for there is record of a coffee house in Istanbul as early as 1511.

Coffee is prepared in many ways in the different countries, and each method of preparation has its earnest proponents who maintain that their way is best. Greeks and Turks prefer strong, sweet coffee sirups, made from boiled coffee. These are sipped relatively cool, after the grounds settle. Syrians add cracked cardamom seeds to the cup of boiled coffee which is further flavored with either rose-water or orange-flower water. Americans and Scandinavians like coffee hot and of medium strength. French and Italians prefer dark strong coffee, made from heavily roasted and finely ground beans. The French, and Americans in the New Orleans area, like coffee best when it contains con-

siderable chicory, which makes for a viscous beverage of full and fruity taste. The French and some Englishmen like "Café au Lait," which is made of equal parts of strong boiled coffee and boiled milk. In some exclusive places, Spanish coffee is served, percolated with boiling milk and containing no water at all. In South American countries, strong coffee extracts are usual, made by continuous percolation. Enough extract may be made up at a time to last for a week. The extract is poured from a cruet into hot boiled milk, for cream is very scarce in those countries. This coffee, while obviously strong, is almost without aroma, causing the common expression among visitors from the North: "The South Americans know how to raise the bean but they don't know how to make a good cup of coffee."

Recently, some fairly good dry coffee extracts have been produced, which yield a beverage on mere solution in hot water, without the need of boiling, drip-brewing or percolation. These extracts have a flavor acceptable to many people, even though they are plainly low in aroma, and are so convenient that they are winning wide acceptance. In some places it is even possible to secure a cup of hot coffee from a slot machine, made from extract, with sugar and cream as desired.

The most important thing about coffee is not how it is brewed, what blend is used, or how strong it is made, but how fresh it is. No coffee is really good that has been exposed to the oxygen of the air for more than a day or two after roasting and grinding, or after the opening of a vacuum-packed container. Coffee extracts also should be relatively fresh when used.

Chocolate is another beverage of great antiquity, which originated in South or Central America. It was first tasted by Cortes when he conquered Mexico, in 1528. At that time, the richer people flavored their chocolate with vanilla and spices and sweetened it with honey or sugar. The liquid was whipped into a froth and drunk with the mouth opened very wide, the better to engulf the delightful foam. Present-day Mexican chocolate is a blend of chocolate and coffee, aromatized with vanilla. "Champurrado" is made from a thin sweetened corn meal gruel called "atole," by flavoring with chocolate, nutmeg and cinnamon.

An important use for chocolate is in soda-fountain drinks, many of which are based on chocolate sirup. Chocolate blends exceptionally well with fruit drinks on the one hand and with milk, malt and ice cream drinks on the other.

Cocoa, which is partially defatted chocolate, is widely used for both hot and cold drinks. Cocoa shells make a cheap beverage roughly similar in flavor to cocoa.

The Indians of the Amazon have another drink, comparable with cocoa, called guaraná, tasting somewhat like coffee, which has been enjoyed locally for a very long time.

Herb and Cereal Drinks

From time to time, various herb teas have been popular, sometimes of necessity, as during the American Revolution, when blackberry leaves, wintergreen (teaberry) and other substitutes were used instead of taxed English teas. While none of the herb teas, or so-called "tisanes," are actively stimulating, they have pleasing flavors. The French country people enjoy vervain tea and peppermint tea. Widely used over all of Europe is linden-flower tea (Tilia). In the Balkan countries, marjoram or sage infusions are used as stomachics, whereas Kat (catha), as also rosemary, infusions are used to combat fatigue. Pleasant tasting drinks are made from chamomile, jasmine, lavender, or dried hollyhock blossoms. Ginger tea, made from ginger and water, with or without milk, was a favorite in this country a few generations ago, as it is in India and many other countries today, often taken "for colds." Catnip tea is a favorite with children.

There are coffee imitations that may properly be classed as cereal drinks. These toasted grain preparations do not resemble coffee very closely although they are satisfactory to some people as a beverage. Decaffeinated coffee has some of the real coffee flavor, but none of the stimulation.

Thickened Beverages

Barley water, a thin gruel made from barley grain, has been used for centuries. It has been popular as a beverage among workers in the fields. The boiling of the water in its preparation has no doubt saved many lives where contaminated water was used. Somehow, a thick drink gives thirst-quenching satisfaction during work in the dust and sun that is not obtained with water alone. The food value is small but perhaps not negligible. Similar drinks are made with rice, oatmeal and flaxseed, as well as with hollyhock flowers (Althaea) and sassafras leaves (filé powder).

In the Balkans, salep, the powdered tuberous root of several varieties of orchid, is used as a thickening agent. On mixing with water and boiling, this powder swells to a thick mucilaginous mass. Salep is used extensively during the winter months, in place of coffee, among people who work outdoors. The drink, Racahout, used by the Arabs of North Africa, is a combination of salep, cocoa, sweet acorns, and potato and rice starches, sweetened and flavored with vanilla.

A delicious cold drink, made of pulverized blanched almonds, sweetened with sugar, is popular in practically every country bordering the Mediterranean. It is the special drink for young girls for such celebrations as weddings and christenings. This milk-like beverage is most pleasant, especially when flavored with anise or angelica. Where almonds are not plentiful, blanched apricot kernels may be used, or the seeds of cassaba or Persian melons, pounded in marble mortars and strained through a fine sieve.

Sirup-Based Beverages

The Koran, the sacred book of the Moslems, specifically forbids the beverage use of alcohol. The command is by no means puritanical and makes no restriction against enjoyment being obtained through beverages, provided they contain no alcohol. The result has been the development of many delightful drinks based on sirups. Most of the sirup drinks, now known the world over, originated in the Mediterranean region. The Arabs, Turks and other peoples of the Near East use many flavors that are uncommon hereabouts, which

might be surveyed with interest. Mere naming of these flavoring substances does not begin to do justice to the delightful sirups that they produce.

SYRUP FLAVORINGS OF THE MEDITERRANEAN REGION

1. Essential Oils	2. Fruits or Flowers
absinthe	apricot
anise	blackberry
bergamot	cherry
cardamom	citron
caraway	currant
cassia	jasmine
cloves	lavender
coriander	lemon
cumin	mulberry
dill	narcissus
ginger	orange
juniper	peach
laurel leaves	pear
lavender flowers	pistachio
lemon	plum
lime	pomegranate
mace	quince
mandarin (tangerine)	raspberry
mint	rose
neroli	strawberry
nutmeg	tamarind
orange	wild cherry
pennyroyal	wild orange
peppermint	
pistachio	
rose	
sassafras	
spearmint	
thyme (origanum)	

Where vanilla is needed, the alcohol-containing extract is not used, but a piece of the bean tied on a string, which may be re-used many times, until it no longer contributes useful flavor. A little licorice powder is sometimes liked. A delightful touch is often produced by the use of a flower water, obtained from flower petals by steam-distillation.

In the Balkans, sirups sometimes are diluted with plain water to make a beverage. Cooling may be done with snow, as is common in mountainous countries everywhere. Often the snow is pounded to high density and stored in caves, protected from the sun. It is transported in the summer in white wool felt bags, often an inch thick, the hard snow blocks being sawed to size. While cold beverages are often sold in stores, along with ice cream and thick, fermented milk products such as matzoon and yogurt, many are dispensed by itinerant merchants. Such a merchant may carry a large polished brass or copper jug on his back containing cold fresh spring water. This he pours from a long spout leading over his shoulder, to dilute the variety of sirups which he carries in small containers in a sort of cartridge belt.

All throuh the South American countries, street vendors prepare iced fruit drinks to order. They grind ice to the consistency of snow, mix fruit sirup with it, compress the mass, and serve it on a stick for convenient "dry drinking."

Juices

In recent years, fruit and vegetable juices have attained great popularity. These have the appeal of pleasant flavor, high food value and a notable content of vitamins. The trend is to drink for breakfast a glass of the juice of orange, grapefruit, prune, pineapple or tomato. Sauerkraut juice is a favorite in Philadelphia. Beautifully clarified apple juice is available and other juices appears from time to time. There is also a "liquefied" apple wherein the pulp is reduced to almost milky fluidity. Most fruit juices are sweet, and are otherwise attractive enough to appeal as a drink at any time through the day.

An Equadorian drink, called naranjilla, is especially delicious, recalling "ground-cherry." This is produced from a tomato-like fruit of golden color that grows on a bush. In tropical and semi-tropical countries many other delicious juices are produced, for immediate consumption, that might be widely popular if means could be found to keep them. These include the rich milky juice of the green coconut, the sweet watery juice of the ripe coconut, date palm juice and sugar-cane juice.

The "Ades"

A class of still drinks, of which lemonade is typical, has existed for a long time, both as the fresh beverage and in bottled form. The best of these drinks have a good proportion of fruit juice plus sugar. Generally, some pulp is included to make the drink cloudy. These items comprise orangeade, limeade, lemonade, as well as "smashes" and punches, all based on citrus fruits. The high acidity impresses many people with their thirst-quenching properties.

A trend has appeared from time to time to omit all fruit juice from the drink and to flavor only with essential oils, plain or terpeneless. This practice has little to recommend it, for the citrus essential oils are irritating, as well as poor-keeping, and should not appear as the principal flavor in drinks. A similar practice is the pulverizing of entire oranges, skin and all, and adding this pulp to sugared water. It is a fair-tasting drink, but far too high in oil and too low in real juice.

Drinks of Animal Origin

Fresh milk is a beverage of high food value that is of enormous popularity, especially with young people. Some think that the great height and vigor of the present generation is due largely to the widespread use of milk. It is not only taken as such, but is used with tea, coffee and cocoa beverages, and with fruit, chocolate, coffee and malt flavors in milk shakes. Combined with cream, eggs and sugar, it appears in ice cream and in the various beverages made therefrom. A childhood drink is "cambric tea," half milk and half hot water.

Fermented milks have been favorite food-beverages for ages. Some, like buttermilk and whey, have had the fat largely removed, but many of the milks soured with special cultures contain all the fat. A well-known example of fermented whole milk is "Bulgarian" or "acidophilus" buttermilk, which was popularized a generation ago, following the publication of Metch-

nikoff's enthusiastic writings. This tart beverage, while thick, is not too thick to drink directly without dilution. Some of the cultured milks, however, like yogurt, matzoon, kumiss and kefir, are so thick that they may be spooned, as a custard, or diluted somewhat with water and whipped, to make a drink called "ta'an." "Cultured buttermilk," available on the American market, is very similar to the Balkan matzoon, though perhaps a bit more tart. Some people like half molasses and half buttermilk as a drink.

In India, a favorite nightcap for children is produced from milk, heated until it develops a yellowish color and a caramel-like flavor.

Beef extracts and bouillons like Bovril, Oxo, etc., make drinks popular in the cold weather. Preparations based on malt, cocoa and milk such as Hemo, Ovaltine and Cocomalt, are food-beverages of considerable popularity. Recently, attempts have been made to push protein hydrolysates, but the strong flavors are against them. Single amino acids, such as glycine, have been suggested as ingredients of beverages.

Clam juice is a food-beverage popular in the Northeast, and a blend of clam juice and tomato juice is a favorite with many in New York City. Clam broth is now obtainable in concentrated form. For those who haven't tested it, we suggest the trial of a cup of bouillon, broth or other kind of thin soup, as a beverage, to go with sandwiches.

* * * * *

This review of the whole field of non-alcoholic beverages has been written to serve as a stimulus for broader thinking on beverage matters. We hope that it will cause initiation of items new to America and the extension or improvement of familiar drinks.

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Methods of Determining the Firmness and Setting Time of Pectin Test Jellies[a]

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The authors review pectin testing methods used in their own and other laboratories, and describe procedures now employed for estimating the setting time and jelly strength of pectins, comparing the results obtained with those secured by other methods. They present a strong case for the Ridgelimeter.

The characteristics of fruit jellies and jams which are of most importance to the consumer are the physical appearance and the taste. Many other physical qualities such as firmness, texture, elasticity, and fracture should, however, be considered if one wishes a complete evaluation of the test jellies involved with pectin standardization. There are two general methods which may be utilized in this particular problem.

The first is to provide some kind of over-all test, preferably simulating actual conditions of use, which integrates the various factors and gives the proper weight to each, but which expresses all this in one numerical quantity or rating.

The second is to follow the more classical scientific method, measuring one factor at a time, and while so doing, eliminate variables by maintaining other factors in non-critical ranges optimum for the single factor being determined.

The completely integrated or over-all test would be without question the easier course for all concerned if only suitable methods could be found which all users and producers would agree properly reflect the utility of the pectin being tested.

[a] Presented before the Eighth Annual I. F. T. Convention, Philadelphia, Pa., June 8, 1948.

This becomes complicated when one considers the great diversity of products into which pectin from a given production batch may be used. Even in the field of use where jelly grade is of prime importance, the pectin may go into pure fruit jellies where the pH varies from 2.5 to 3.4, or into baker's type jellies where no fruit is used and where glucose supplants sucrose and the pH is usually below 2.5. Pectin from the same batch might possibly be sold to a confectioner who uses it in 80-83% sugar jellies with varying acidities and buffer contents. Finally, part of that same pectin shipment may go into the production of household pectin packages, which in itself is a highly complex field of use.

Thus it is evident that the "use test," for a large scale producer of pectin, is hardly in the realm of practicability, even if one considered only the preserving industries as users of pectin. In fact, the preserver who uses pectin for more than one specific product could easily get into difficulties with his own pectin stocks if they had been separately standardized for several different uses. It has seemed logical to us that uniformity in the general jelly-making characteristics of pectin was of the utmost importance to the preserver and that the least complicated methods possible should be used in insuring that desirable uniformity.

It was only after approximately twenty years of continual search that the California Fruit Growers Exchange laboratories gave up the quest for the integrated physical or use test and adopted the individual tests. Jelly firmness was selected as the most necessary and important individual factor for standardization. The

goal was to test precisely and reproducibly the jelly firmness which a given pectin is inherently capable of producing under standardized conditions which could be easily maintained in non-critical ranges. Further, the firmness determination should require only rugged, inexpensive equipment and the test must not be time consuming.

Special test jellies need not, of course, be salable fruit jellies made under conditions identical with those of any user. Instead they have been designed to determine most accurately the one thing, jelly grade as to firmness, under controlled laboratory conditions. Should this scientific approach require further justification among technologists, consider a field other than our own where we will be less apt to have fixed ideas. Portland cement is tested for tensile strength by molding cement paste into standard briquettes, curing these in moisture-saturated air the first day and thereafter under water until they are to be broken in the testing machine. Certainly no one uses cement in just this way but all users and producers are benefited by this test which is much more precise and reproducible than would be the case if actual conditions existing in reinforced concrete construction were approximated for this tensile test of cement.

Two broad possibilities are open for testing jelly firmness. The jelly may be subjected to conditions so as to exceed the elastic limit whereby it will be permanently deformed or actually ruptured, or the tester may be such that the jelly will undergo no measurable permanent change during the test procedure. The literature on these types of testing methods is quite extensive and need not be reviewed here.

Our work has indicated that tests involving permanent deformation or rupture of the jelly are influenced by a variety of factors, each perhaps of some importance but not capable of easy control or separate evaluation. These factors are generally highly dependent upon slight variations in manipulative technic during jelly preparation and testing and their combined effects are quite apt to be confusing. Testers which operate within the elastic limit of the jelly are free from many such influences.

The trend of our work on this problem has been to refine the jelly-making method which was devised here with the assistance of H. T. Leo and was first published by Wilson *(16)* twenty years ago, then to develop the Lockwood and Hayes "Ridgelimeter" *(8)* into what is now widely known as the Cox-Higby "Exchange Ridgelimeter" *(3)*. It became necessary, along with these developments, to provide a laboratory control method for the standardization of slow and rapid setting pectins, types now commonly known by pectin users throughout the world. Since the setting time of pectin jellies may influence the grade testing methods it is desirable to consider the setting time factor before discussing the preparation and testing of sugar-water-pectin jellies.

Cole, Cox and Joseph *(2)* in 1930 showed that the rate of gelation of pectin jellies, commonly referred to as the setting time of the pectin, could have a profound influence upon the results obtained by certain laboratory testing procedures. Olsen *(10)* later published results which confirmed this contention regarding setting rate and jelly firmness. When he used a relatively slow-setting citrus pectin he found it desirable to use a large, fixed amount of acid in the test jelly, so that the pH was about 2.2. His data show that the Tarr-Baker tester readings in a 65% sugar test jelly remained practically constant from a pH below 2.0 up to about 2.7. His jellies were made by holding the pectin constant and varying the amount of acid which was added along with the pectin. If Olsen had used a very fast setting pectin he would have found a loss in jelly strength at the higher acidities, due to the fact that by his "short-boil method," the acid was present all during the cooking period and premature gelation was taking place.

A later publication by Stuewer, Beach and Olsen *(15)* illustrates how the so-called optimum pH method of making test jellies can be very misleading. Their curves for the effect of pH on jelly strength for apple pectins show a very definite optimum jelly strength near pH 3.1 with rapid decreases in strength at both higher and lower acidities. One might conclude, from those curves, that the way to get full value from the pectins would be to use them only at pH 3.1. This would also be a good argument for using a pH 3.1 buffer solution in the test jelly so as to maintain the system at the peak of its sharp optimum strength curve. Those authors realized, however, that the setting rate of the jellies, when acid was present in their test batches, became an important factor. Their curves comparing the short-boil and excess-acid methods for apple pectin jellies clearly prove that there is no optimum pH for the apple pectins when premature gelation is avoided by having the setting acid in the glass, as recommended by Wilson *(16)* six years earlier. Their jelly strength curve, when using the excess acid method, shows a jelly strength practically identical with that indicated by the peak of the optimum pH curve, and furthermore, the strength remains constant at this level from pH 1.9 up to about 2.8, where a decrease starts in both curves. The authors stated that, "Observations made here indicate that most of the difficulties involved in the routine evaluation of apple pectin jellies may be obviated by the simple expedient of preparing the jelly mixture without acid, adding an excess of acid to the glasses, and pouring the jelly mixture into these at exactly 96° C." These conclusions regarding the best method for grading apple pectins apply to the method our own laboratories have used with citrus pectins for the past quarter century.

Exchange Method for Grading Pectin

Preparation of Jellies. The method described in 1928 by Wilson *(16)* was given in more detail in 1944 by Cox and Higby *(3)* when they discussed the "Exchange Ridgelimeter" for testing pectin jellies. The actual directions for preparing the test jellies, as described in our book of standard methods, are considerably more specific than is indicated by the Cox and Higby description. A copy of the fully detailed method has been furnished to the Research Committee of the National Preservers Association and would be given here except for

space limitations. There are some amplifications to the 1944 version, however, which should be listed here.

The pan specified in the detailed method is a 4-quart stainless steel saucepan. Actually a 3.5 quart size, stainless steel or aluminum, would suffice. The pectin-sugar dispersion mixture is added to the distilled water all at once with vigorous stirring and then is allowed only a 30 second period before being placed upon the fire. The fire is so adjusted that the total heating time for the 1200 gram batch of jelly should not exceed 6 minutes. After the batch is cooked to weight and removed from the fire, the pan is tipped slightly so the liquid nearly overflows. A thermometer is put in the batch and when the temperature has dropped a degree or two, the surface of the solution is scraped free from any scum of bubbles which may form. Just as soon as the temperature reaches 95° C. the batch is poured. The first glass, a regular Hazel-Atlas No. 85 tumbler containing 2.0 ml. of preserver's acid (376 grams tartaric acid per liter of solution) has previously been placed in the setting time apparatus as illustrated in Figure 1. The remaining

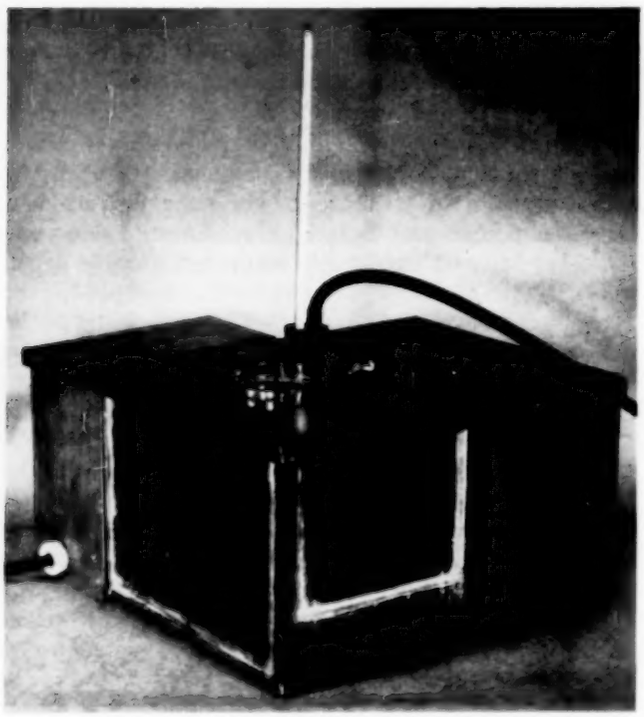

FIG. 1. Water bath apparatus used for determining setting-time of pectin test-jellies at 30° C.

three glasses are the calibrated ones furnished with the instrument and which have been fitted with paper "sideboards" as mentioned in the Cox-Higby *(3)* article. The sideboards are made by using ¼ inch gummed paper tape and allowing ½ inch to project above the glass. These latter three glasses should contain 2.6 ml. of the standard acid solution since their volume has been increased by the "sideboards."

A glass rod in the tumblers will permit stirring as the batch is poured but, as Olsen *(11)* has pointed out, stirring in the glasses is not necessary if one pours very rapidly. The glasses should be filled to the top of the "sideboards."

Determination of Setting Time for Pectin Jellies. Although the setting time of pectins has been mentioned in pectin literature for about two decades, we have seen no precise method given for its determination. Olsen, Stuewer, Fehlberg and Beach *(12)* in 1939 described what they termed a quantitative method. We believe the method which our laboratories have used since 1937 permits more precision and should be described in this connection.

The apparatus used is illustrated in Figure 1. It is a water bath having glass windows on opposite sides and a support for a jelly glass placed between the windows so that when the tank is filled to the overflow outlet with distilled water at 30° C., the jelly glass is surrounded with water almost to the top and is held in place by a clip provided for the purpose. The light placed behind the rear window enables one to observe the jelly through the front window. Circulation of the water is obtained by a slow stream of air bubbling beyond the field of vision between the two windows. Temperature adjustment of the bath for subsequent batches may be made easily be adding water of the proper temperature. The 30° C. level chosen is such that radiation cooling is almost off-set by heating due to pouring the hot jelly.

The jelly batch is poured as has been described above. A stopwatch is started just as soon as the first glass is filled and then the remaining glasses for Ridgelimeter testing are poured rapidly. Close attention must then be given to the first glass which is in the 30° C. water bath.

The glass in the water bath is given a slow, easy twist at intervals, and observed through the window in the front of the tank. The set will be seen to progress from the bottom to the top of the jelly. At first, the particles of jelly will be seen to rotate only in the direction in which the glass was turned. As the jelly starts to set, it will be seen that the jelly particles in the lower part of the glass will rotate first in the direction in which the glass was turned, and then will move back in the opposite direction. The watch is stopped when the last portion of the jelly at the top of the glass can be seen to move back in a direction opposite to that in which the glass was turned. The interval between the starting and stopping of the watch is the setting time of the jelly, usually referred to as the setting time of the pectin.

The so-called setting times of most commercial pectins, in the 30° C. bath and at pH values between 2.2 and 2.4, will be less than 5 minutes. The relation between setting times at 30° C. in the water bath and in air at 20-25° room temperature, is shown by Table 1.

The setting times shown in Table 1 pertain, of course, to the specific test jellies involved and to their pH and sugar concentration. It is obvious, as Leo, Taylor and Lindsey *(7)* have stated, that as the pH of the test jellies is raised, these setting times would become longer. However, contrary to the contention of those workers, pectins do have inherent properties affecting the rate of set of their jellies when measured at fixed conditions of temperature, sugar concentration, and acidity *(4)*. For instance, when using the standardized jelly making technic just described, Exchange slow-setting pectins

TABLE 1

Relation Between Times of Set for Exchange Standard Test Jellies, in Air at Room Temperature and in a Water Bath at 30° C.

Setting Time in Minutes	
Air at 20-25° C.	Water Bath at 30° C.
1.00	0.90
2.00	1.65
3.00	2.25
4.00	2.80
5.00	3.25
7.00	4.00
10.00	5.10
14.00	6.30

produce jellies whose setting times, by the present method, fall within the band of 3.25 and 4.00 minutes, while under the same conditions rapid-setting pectins set as rapidly as 0.10 minutes. The preserving industry is well acquainted with the characteristic difference between the behavior of these two types of pectin when used in juices and at higher pH levels.

Determination of Jelly Firmness with the Exchange Ridgelimeter. The Ridgelimeter used for measuring the firmness of test jellies is shown in Figure 2. The details

FIG. 2. The Exchange Ridgelimeter, showing a jelly in the measuring position. Calibrated glasses are shown with and without "sideboards."

of operation for this instrument have been published by Cox and Higby *(3)* and additional information about the preparation of jellies for the standardized test have been given in this present paper. Our original publication on the Ridgelimeter did not emphasize the importance of checking the scale of the instrument occasionally, especially if new glass plates were substituted for those originally furnished.

An excellent checking gauge can be made by cutting a ¾ inch stainless steel rod to exactly 2.50 inches in length. When this rod stands on the glass plate and the point of the micrometer screw just touches its top, a scale reading of exactly 20.0 should be obtained. If the reading is not 20.0 the vernier and scale can be adjusted so as to produce this reading by using the set screws provided on the instrument. It has been found that the best results are obtained when the tip of the micrometer screw is about 1.0 mm. in diameter.

The calibration curve which we use for the instrument in grading regular pectins (both slow and rapid setting) is reproduced in Figure 3. This curve shows that we consider a sag of 23.5% to be normal, as was mentioned by Cox and Higby *(3)* in 1944.

The curve of Figure 3 does not apply to the grading of low methoxyl pectins. This of course is to be expected since the rheological properties of the two types of gels

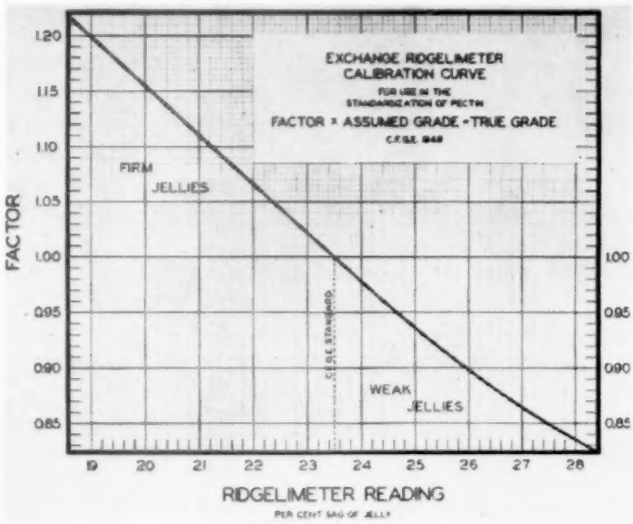

FIG. 3. Calibration curve for regular citrus pectins graded by the Exchange Ridgelimeter.

are different, as has been shown by Cheftel and Mocquard *(1)*. The curve used in our laboratories for the standardization of low methoxyl pectin is nearly parallel to the one of Figure 3 and crosses the line of factor 1.00 for normal firmness, at 20.5% sag. The gel batch for testing low methoxyl pectin is entirely different from that used with regular pectins, and is described elsewhere *(5)*.

Discussion

The subject of the present symposium, "Pectin Standardization," implies the comparing of pectins with some standard, or actually it means the insurance or guarantee of uniformity. The actual choice of a "standard" for pectin jellies has been considered by some as a difficult problem. We believe that uniformity in jelly strength is of the greatest interest to the preserver or jelly maker and that the Exchange Ridgelimeter with its easy and precise measure of jelly firmness permits the standardization of pectin to a uniform jelly grade.

The standard of firmness we selected for calibration purposes, a sag of 23.5% for the particular test jelly described here, was based upon twenty years experience with hand grading of jellies which the preserving industry considered normal. Owens and Maclay *(13)* in 1946 stated that:

> "The value of 0.235 for the unit compression used as the standard of firmness by Cox and Higby yields a value of about 3 g./cm.^{2} for the shear modulus. It might be well for the industry to consider some such standard value with a standard procedure, in order to establish objective standards by which pectin may be sold. From the work presented here, a more reliable measurement would result if a slightly stiffer gel were chosen for the standard. A value of 4 g./cm.^{2} would be more desirable."

However, a year later Owens, Porter and Maclay *(14)*, while discussing the grading of pectins and the use of certain instruments for that purpose, stated that "A shear modulus of 3 g./cm.^{2} was chosen as a standard, and the results suggest that it be considered by the pectin industry as a basis for grading their commercial products." This value for the shear modulus coincides with the 23.5% sag which had been chosen by us as representing a standard jelly.

The pectin literature reveals many arbitrarily chosen technics for making test jellies with pectin. However, since the main concern now seems to be standardization, it is evident that some basic technic should be accepted for preparing the test jellies, rather than some specialized technic which may apply only to one narrow field of use. The aqueous phase of test jellies should be distilled water which would contribute nothing to aid in jelly formation. If a pectin would form a satisfactorily firm jelly with water, sugar and acid, it is well known that its jelly forming ability would be enhanced by the use of fruit juice instead of water. This would, of course, be to the advantage of the preserver making fruit jellies and jams. Since commercial jelly products containing pectin vary in pH from 2.0 to 3.5, and since it has been shown by Olsen *(10)* and his associates and by hundreds of our own tests, that there is a region of constant jelly strength for water jellies at pH 2.2-2.4, there seems no reason for wishing to get out of that pH region in making test jellies. Lampitt and Money *(6)* in 1937, using a tester with a vane inside the jelly, found that the jelly strength was practically constant from pH 2.0 to about 3.0. They studied testers which broke or tore the jelly and reported that "None of these methods appears to be measuring the 'true' strength of the gel." Test jellies at higher pH regions, even in the presence of "artificial juices," are subject to influences which should be avoided in choosing a basic recipe for use in insuring uniformity or standardizing. Twenty-five years ago Macara *(9)* showed that pectin jellies at high pH, particularly with fruit juices, were very slow to attain maximum firmness. He pointed out that high acid was useful in hastening development of maximum firmness. This factor is of great importance to pectin producers where dozens of pectins must be graded daily and where factory production must not be delayed by unnecessary jelly testing complications.

Finally, it is our opinion that the test jelly should be made with water, should have sugar at 65% concentration, and with acid in the glasses to bring the final pH down to 2.2-2.4. The instrument for grading should be rugged, inexpensive, simple in design, easily and quickly operated. It should operate within the elastic limit of the jelly. The Exchange Ridgelimeter seems to meet these qualifications although in common with most others, this instrument does not lend itself to measuring the sag in jellies previously "set" in other than the standard containers. Owens and Maclay *(13)* in comparing the Ridgelimeter with the Tarr-Baker tester type and with their own rather complicated "Rigidometer," show that the Tarr-Baker tester gave results on duplicate gels varying as much as ± 5% while the other two instruments kept these variations within ± 2%. Owens, Porter and Maclay *(14)* later reported that the Tarr-Baker instrument "was more time consuming and less reproducible" than their Rigidometer and the Exchange Ridgelimeter. They renamed this latter instrument "Sagometer" to avoid confusion with the name of their own instrument which they had subsequently devised. Referring to the Ridgelimeter, therefore, they say, "The Sagometer which measures percentage sag of a gel is rapid and precise, and can be calibrated against the rigidometer to give values for the shear moduli."

More than fifty Exchange Ridgelimeters are now in use, outside our organization, in this country and abroad. Although this fact leads us to believe that the instrument and method as here described meet practical requirements, we are still alert to any possible improvements.

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Grading Pectins[a, b]

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A comparison is presented between the use of acid during the preparation of test jellies for grading, and the use of salt mixtures for this purpose. Synthetic juice buffer salt solutions are described as preferable since they more nearly resemble the actual products.

A study *(1)* has just been completed which indicates that more emphasis is needed upon the preparation of test jellies for grading purposes than upon the method of testing. Two types of measurement, breaking strength and sag, were made in this study of grading and two methods of adding acid, in the glass and before boiling, were employed. Buffer salt solutions were also used in one phase of the study. Certain of these phases of study appear to have produced results which warrant presentation in a symposium on "grading."

This paper will consider two questions: (one) "Should acid be present during the preparation of test jellies for grading?" and (two) "Should salt mixtures be used in jellies for this purpose?" The paper will present a comparison of the results of the two types of measurement upon jellies made by the two methods of adding acid over a pH range 3.5 to 2.5, or 2, as the case may be, in the presence and absence of buffer salts.

Should Acid Be Present During Cooking Period?

This question has been considered by others in the past *(2, 5, 7)*. For instance, the point has been made by Stuewer et al. *(7)* that the "excess-acid" method of grading, where an excess of acid is placed in the glass, is more simple because it eliminates the complication of first determining the optimum pH of gelation. Actually this pH is of negligible importance because pectin manufacturers have standardized production methods which allow them to predict quite closely the optimum conditions of acidity for gelation. If necessary, they could illustrate the trend of curves for elasticity or breaking strength of jellies, cooked with and without acid, from the various types of pectins they produce with a fair degree of accuracy. These curves would appear to be of value to the trade in deciding which pectin to choose for a certain job, or for continued assurance in the uniformity of the product. A few tests would soon indicate to the pectin producer whether his product was showing variations from normal as to optimum pH for gelation, sag, etc. This would obviate the necessity for determining the effect of small increments of acid over a wide range of acidity in the case of each and every pectin. In this, study, however, the interest is in what happens to the physical characteristics of sag and breaking strength when the acid is present or absent during cooking.

When the effect of the manner of introducing the acid upon jelly strength and sag was studied upon jellies containing 0.67 percent commercial apple pectin, results were obtained as in Figure 1. Point-to-point curves are drawn to better indicate variations in breaking strength. The solid line indicates that a smooth, typical jelly-strength curve will be obtained when various amounts of acid are present during the cooking period. Again, a uniform curve (long dashes) is shown for sag measurements upon the jellies cooked with increasing amounts of acid. On the other hand, more erratic results were obtained from both strength (short dashes) and sag measurements (dot-dash) upon jellies produced by pouring, with rapid stirring, hot sugar-pectin mixtures upon varying amounts of acid placed in the jelly glasses. While the trend is toward gels of lower strength as more acid is present, the strength under the conditions of the "excess-acid," which adjusts the pH of the jelly to 2.07, would not appear to be satisfactory for grading purposes. Sag at pH 2.07 of the jelly made by placing the acid in the glass compares favorably with the sag at pH 3.1 of the jelly made by a 4.5-minute cooking with acid (normal boil procedure), however, this is thought to be largely a matter of chance.

Contrary to the results shown by Figure 1, for a rapid-set apple pectin, results obtained upon jellies containing 0.50 percent of a slow-set citrus pectin shown in Figure 2 would seem to indicate that jellies for grading by means of strength measurements might be made either by cooking with acid (solid line) or by pouring the hot sugar-pectin mixture into acid in the glass (short dashes). The strength value used for grading could be either that at the optimum pH (2.85) or that made with "excess-acid," at about pH 2.1, without being too far out-of-line, provided the proper factor be used for aligning the two sets of results. The slow-set citrus pectin differs from the rapid-set apple pectin in the degree of coagulation or pregelation which takes place during about 4.5 minutes of cooking with acid. No pregelation occurs when cooking gels containing the slow-set citrus pectin; the slight decrease in strength as more acid is added is due to hydrolysis. Sag measurements upon the jellies where the acid has been added to the glass show uniform values below pH 2.75 (dot-dash) and these could be readily adapted for grading this type of pectin, but less uniform values (long dashes) were obtained where the acid was present during cooking.

Figure 3 illustrates that when acid is present while cooking the jellies containing 0.57 percent of a citrus rapid-set pectin, the breaking strength reaches a maximum at pH 3.15 and decreases gradually, but uniformly, as more acid is added (solid line). When the acid is present in the glass and the other ingredients, which have been cooked, poured thereon, fairly uniform values

[a] This paper consists largely of data and discussion taken from a more extensive study on grading of pectins which will be published as Bulletin 272 of the Delaware Agricultural Experiment Station.

[b] Published as Miscellaneous Paper No. 52 with the approval of the director of the Delaware Agricultural Experiment Station. Contribution of the Department of Chemistry, May 7, 1948.

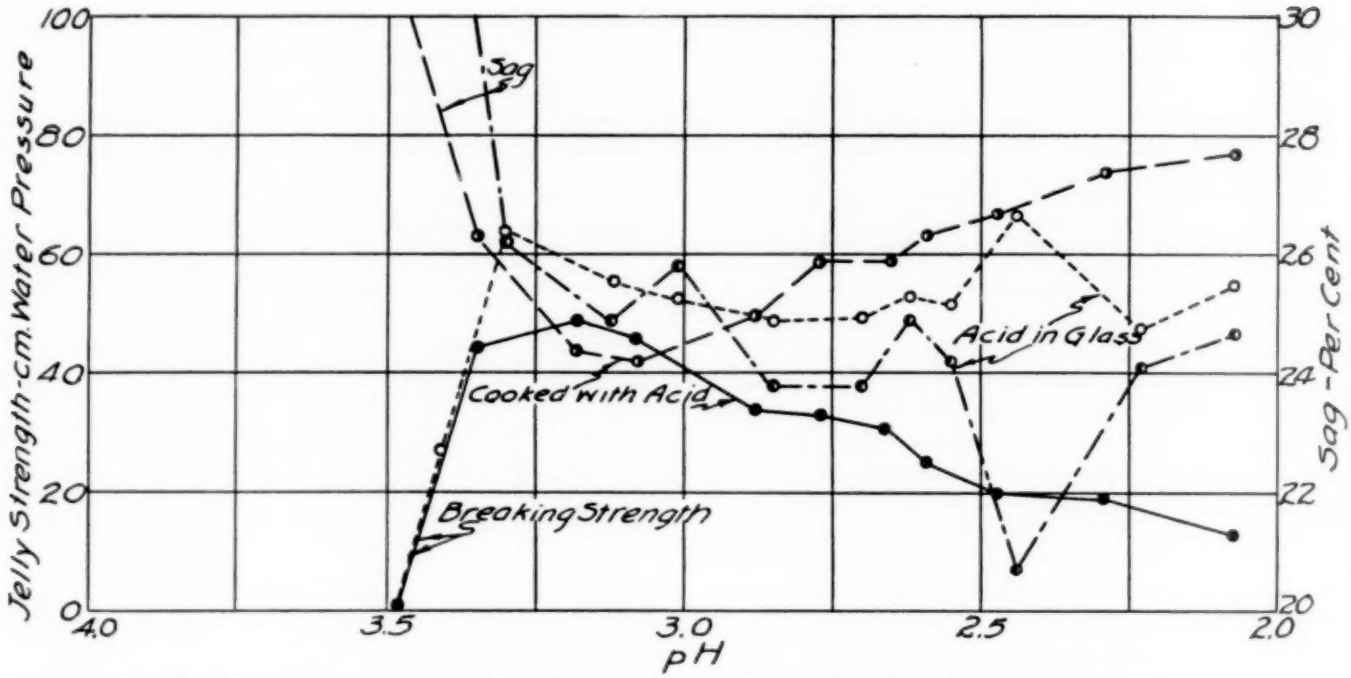

FIG. 1. Effect of adding acid before and after cooking on jelly breaking strength and sag—apple pectin.

are obtained for breaking strength as higher concentrations of acid are present until the point is reached where coagulation tendencies are paramount (short dashes). When the acid is added in the glass, the tendency is for the strength to be much greater at the lower pH values, than the strength in the normal pH range of gelation (3.0 to 3.3) in commercial usage. Also, the strengths are much greater than by the "normal-boil" procedure (solid line). If sag measurements are made upon jellies containing this same citrus pectin more uniform results are obtained when the acid is present during cooking. The broken line in Figure 3 shows that while a fairly regular curve is obtained, any grade determination at pH 2.1 based on the sag measurement would be out of line with a grade determination at pH 3.

In summarizing, it is indicated that grading could be based on both jelly strength and sag values in the case of the apple pectin when acid was present during cooking, but not when acid was placed in the glass and the rest of the jelly mixture poured into it. In the case of the slow-set citrus pectin it would appear that the jelly strength measurement may be used in grading with either method of making the jelly and, while there might be some question on the use of sag measurements in the

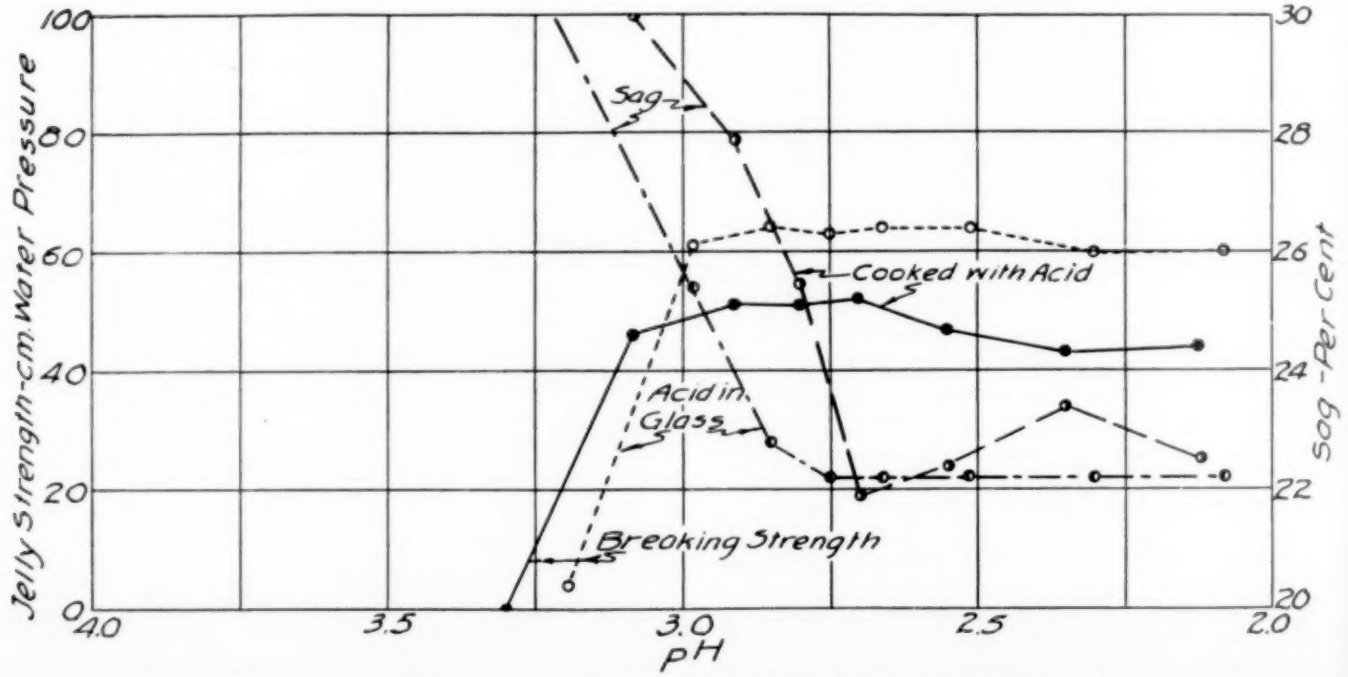

FIG. 2. Effect of adding acid before and after cooking on jelly breaking strength and sag—citrus slow-set pectin.

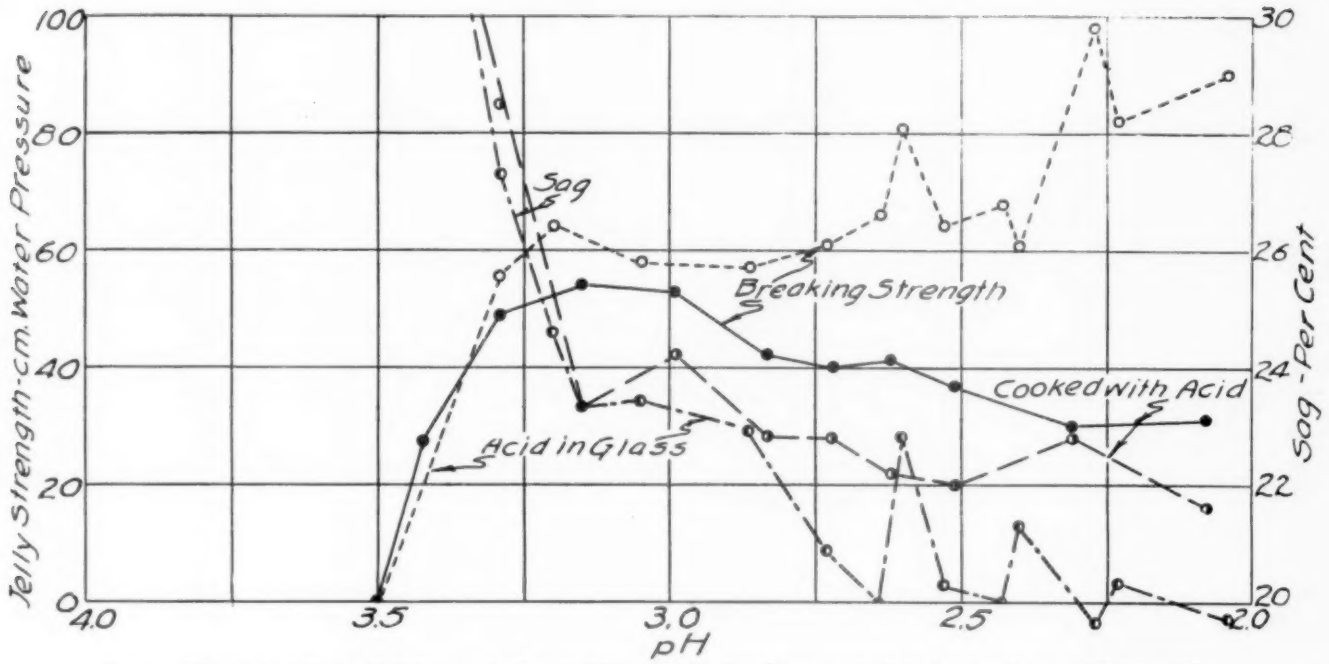

FIG. 3. Effect of adding acid before and after cooking on jelly breaking strength and sag—citrus rapid-set pectin.

case of the jellies cooked with acid, apparently sag measurements can also be used. However, in the case of the fast-set citrus pectin, the results would indicate that breaking strength alone should be used in measurements for grading pectins of this type. Only the jelly strength measurements upon jellies made where acid was present during cooking may be considered satisfactory as indices for grading purposes in the case of all three pectins. The results indicate that both the method of measurement and the method of making the sample gels influence results. Obviously, something must be done differently in order to obtain a better correlation of results.

Should Salt Mixtures Be Present During Grading?

Olsen et al. *(6)* claim the so-called optimum pH can be modified through use of a synthetic juice, a mixture of buffer salts and acids which represents the average analysis of a series of strawberry juices. The composition of their mixture follows:

Potassium Phosphate	1.535g
Potassium Citrate	6.33
Sodium Citrate	0.985
Calcium Citrate	1.19
Magnesium Acetate	2.02
Citric Acid, anhydrous	25.00
Sucrose	40.00
Water to make one liter.	

Despite the conclusion of Olsen et al. *(6)* that the preparation of jellies containing these salts and 65 percent soluble solids at pH 3.1 is completely satisfactory, it was decided to determine the effect of variation of pH over the range 3.5 to 2.5 using the same three pectin samples discussed in the last section.

The results of preliminary study were so promising that it was decided to make a more detailed examination of the effect of a salt mixture, similar to that of Olsen et al. *(6)* with the exception that less citric acid (17g.) was used in order to adjust the pH to 3.5. Following this, there were added increments of acid (0 to 5ml. 50 percent tartaric) to provide a series of jellies in the pH range 3.5 to 2.5. (Magnesium tartrate was used in place of magnesium acetate through error).

The pectin was dispersed in two liters of the salt solution as a 1.0 percent solution in the case of the apple pectin; as a 0.75 percent solution in the case of the slow-set citrus pectin; and as a 0.85 percent solution in the case of the rapid-set citrus pectin. This was done by mixing the necessary pectin in each case with 100g. sucrose and then dispersing the mixture in the synthetic juice and diluting to two liters. This made a sugar-salt-acid-pectin mixture containing about 12 percent soluble solids. Two series of jellies were made for each pectin. The pH of one series was adjusted to vary between 3.5 and 2.5 before cooking and each jelly was boiled to 150g. final weight; in the other series, each jelly was boiled to 145g. (about 67.2 percent soluble solids) in order that the final weight would also be 150g. when the cooked sugar-pectin juice concentrate was poured on the 5 ml. of acid solution of varying strength in the glass. The strength of the acid solution was varied according to the desired pH. Each jelly was made as follows: Sucrose, in an amount sufficient to raise the total solids added to the jelly mixture to 97.5g., was placed in a one and one-half quart sauce pan; acid was added; water was added sufficient to adjust the original weight to a uniform value; then the jelly mixture was boiled to 150g., or 145g., as the case may have been; and, finally, the jelly mixture was poured into standard 5-5/32 ounce, Hazel-Atlas No. 2750 tumbler-shaped jars. In the series of gels where 5.0 ml. of acid solution was present in the glasses, the other ingredients, properly concentrated, were poured into the acid and the whole stirred with a glass rod for 15 seconds. After skimming,

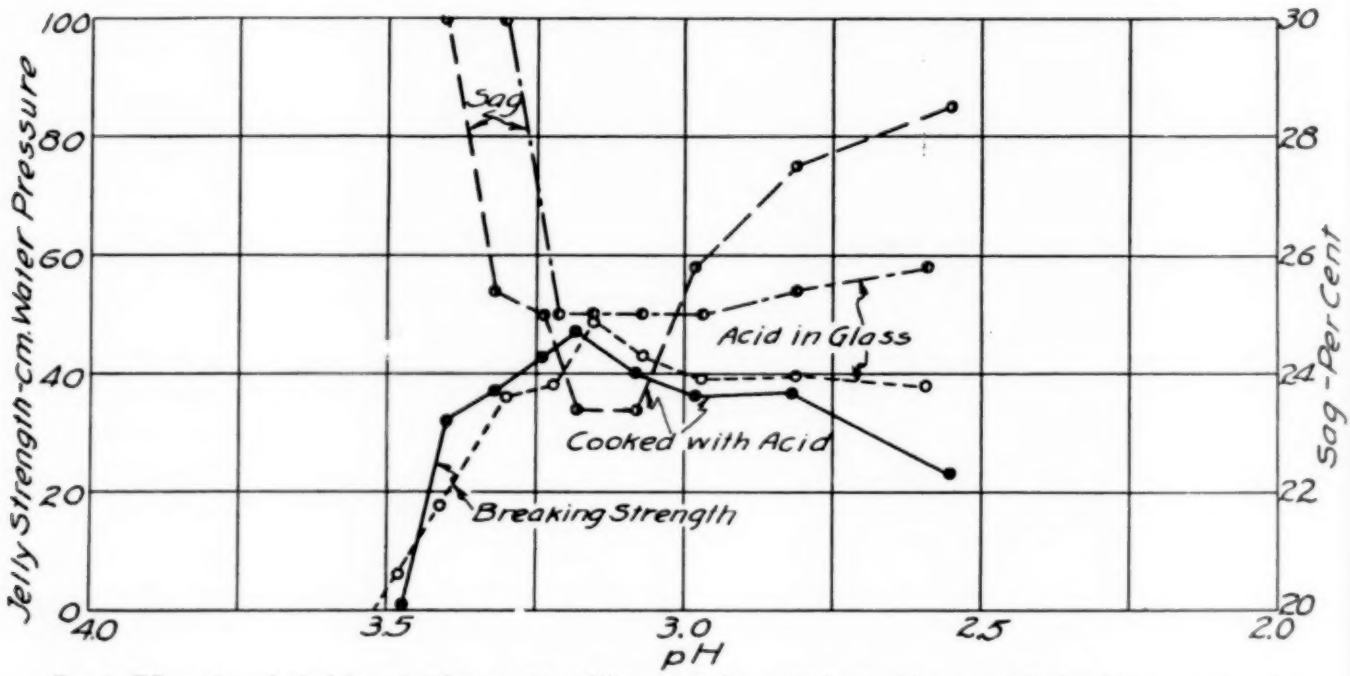

FIG. 4. Effect of synthetic juice salt mixture when adding acid before and after cooking upon jelly breaking strength and sag—apple pectin.

the jellies were held partially immersed in a water bath at 26° C. for 20 hours. The jelly strength was measured while the jelly remained in the glass, the jelly was then turned from the glass and the sag measured with the Exchange Ridgelimeter but not according to Cox and Higby's *(3)* directions because of insufficient jelly volume. In the modified method, a standard block was used under the glass plate in order to raise the jelly sufficiently to measure with the adjustable screw of the Ridgelimeter. Sag was calculated in accordance with the method of Lockwood and Hayes *(4)*; the original height of the jelly in the glass was measured, the height of the jelly after two minutes from the time it was turned out of the glass was easily measured from the screw setting on the Ridgelimeter, and the percentage of sag was calculated from the difference. The jelly was returned to the glass and the pH measured using a glass electrode. Jelly breaking strength and sag values appear plotted against pH by the point-to-point method in Figures 4, 5, and 6 for jellies made from the three pectins in the same order as they were previously tested.

The curves in Figure 4, indicating the data taken upon jellies made with the apple pectin, differ from those in Figure 1. Where the acid was present during

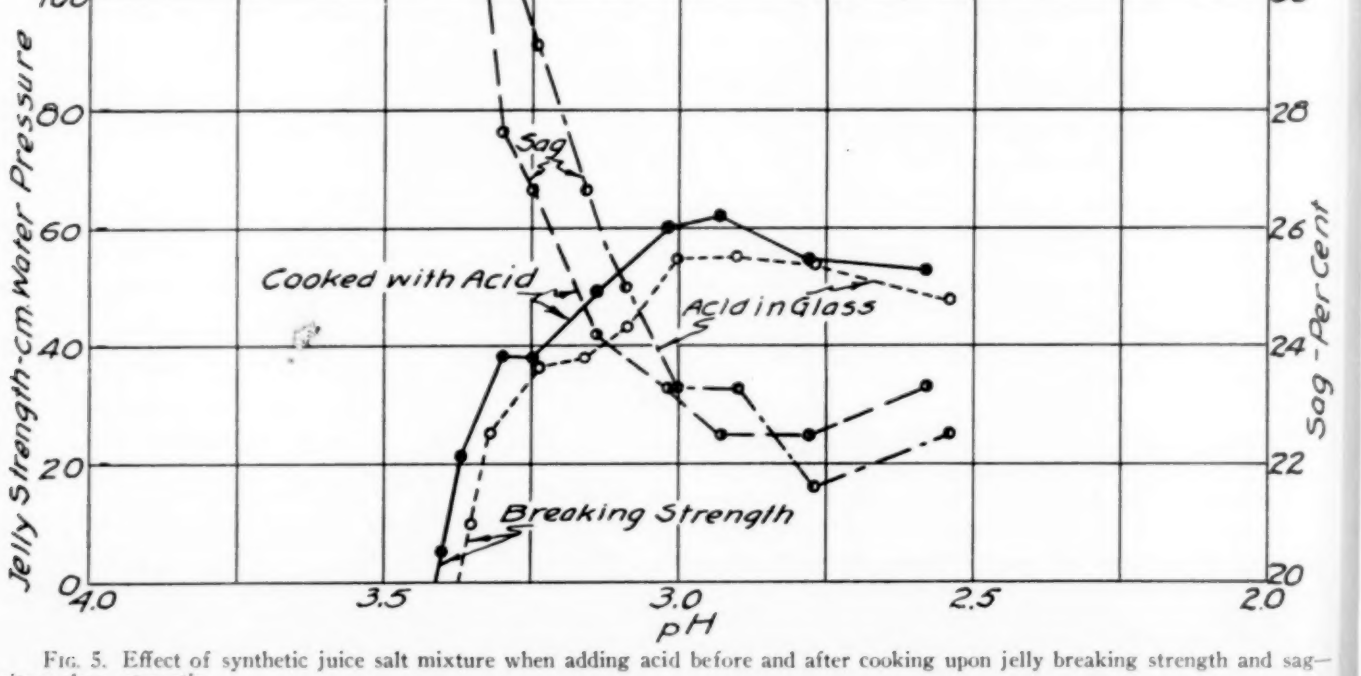

FIG. 5. Effect of synthetic juice salt mixture when adding acid before and after cooking upon jelly breaking strength and sag—citrus slow-set pectin.

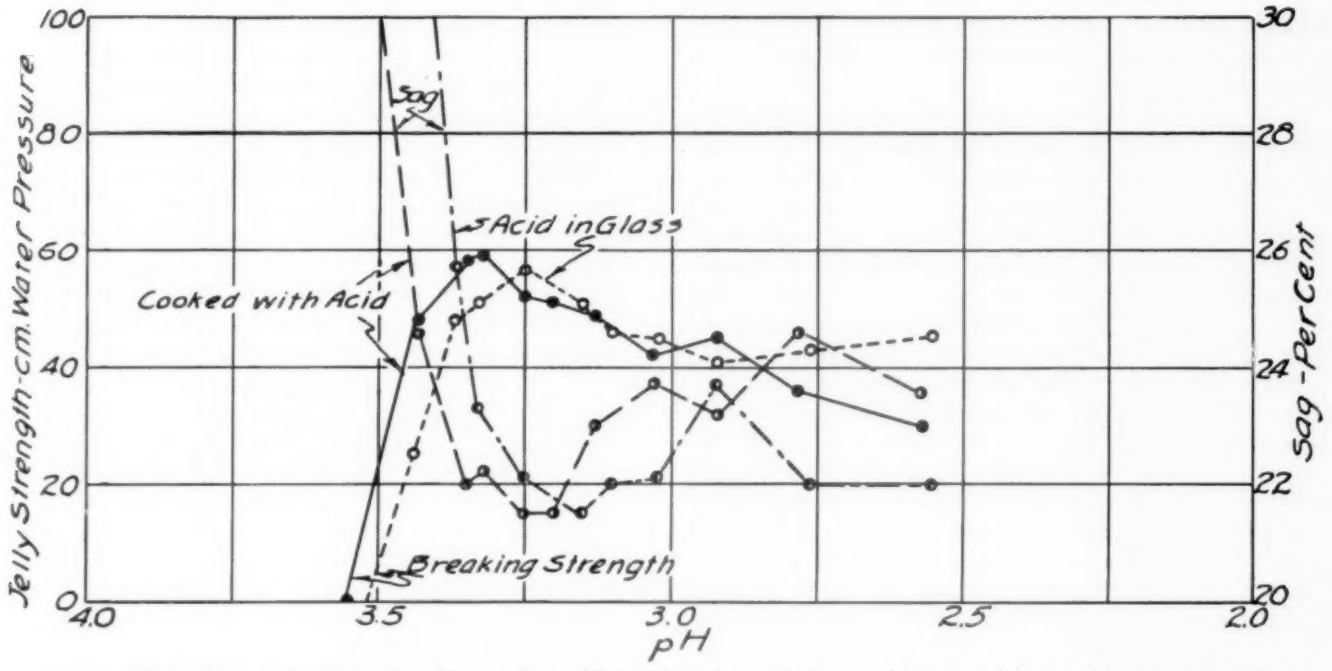

FIG. 6. Effect of synthetic juice salt mixture when adding acid before and after cooking upon jelly breaking strength and sag—citrus rapid-set pectin.

the cooking of the jelly, the lines follow the same general trend in both figures. There is an optimum pH of gelation and then the strength (solid line) decreases gradually. Sag (long dashes) increases with increased acidity somewhat more rapidly in the presence of the high concentration of salt. Contrary to the values indicated in Figure 1, the data illustrated in Figure 4 for jellies made by pouring the hot, concentrated jelly mixture upon the acid in the glass show closer agreement with the values for both strength and sag obtained on jellies made with acid present during cooking. When the acid is in the glass, a similar type of curve is obtained for both strength (short dashes) and sag (dot-dash), after the optimum strength is reached the values decline gradually as the acidity is increased.

The strength values for jellies made with the slow-set citrus pectin are also very nearly the same when the synthetic juice was used (Figure 5) whether the acid was present during cooking (solid line) or added later by having it in the glass (short dashes), the former being found slightly stronger. On the contrary, in the absence of buffer salts, it will be recalled that higher strengths were obtained if the acid was added in the glass. The curves for both sets of the sag measurements are somewhat more uniform when salts are present, but show much less sag at higher pH values, Figure 5, than in their absence, Figure 2. In other words, the initial pH of gelation is raised by having the high concentration of salt present.

The value of the presence of the buffer salts is shown again when the jellies are made from rapid-set citrus pectin. The curves in Figure 6 show a slight increase in the initial and the optimum pH when both strength and sag measurements are considered. The greatest strength

TABLE 1

Effect of Synthetic Strawberry Juice (Buffer Salt Solution, pH 3.5) upon Grading Values

Sample	Conc. of Pectin in Jelly, %	Method of Adding Acid	No Buffer Salt				Buffer Salt Solution, pH 3.5			
			Optimum pH	Jelly Strength, cm. H_2O Pressure	Sag %	Grade (Based on Strongest Gel)	Optimum pH	Jelly Strength, cm. H_2O Pressure	Sag %	Grade (Based on Strongest Gel)
Apple Pectin	0.67	Present during cooking	3.18 3.08	49	.... 24.2	96 93	3.18 3.18	47	.... 23.4	95 99
		In glass	2.44 2.44	67	.... 20.7	116 109	3.15 3.22	49	.... 25.0	96 92
Citrus Pectin (Slow-set)	0.50	Present during cooking	2.70 2.70	52	.... 21.9	133 139	2.93 2.93	62	.... 22.5	146 136
		In glass	2.85 2.75	64	.... 22.2	148 138	3.00 2.77	55	.... 21.6	137 140
Citrus Pectin (Rapid-set)	0.57	Present during cooking	3.15 2.08	54	.... 21.6	119 123	3.32 3.25	59	.... 21.5	125 125
		In glass	2.27 2.27	98	.... 19.5	164 135	3.25 3.15	57	.... 21.5	123 125

and the least sag are practically the same whether the acid is present during or added after cooking the jelly mixture.

It may be interesting to consider the grades which would be assigned these three pectins as a result of the highest jelly strength and the lowest percentage of sag for the jelly at the optimum pH of gelation with and without the presence of the synthetic juice mixture. Table 1, presents the optimum pH of gelation, highest strength value of any one gel, lowest percentage of sag of any one gel, and the calculated grades of the three pectins as determined by using established factors for standard gel strength *(1)* or by the method of Cox and Higby *(3)*. Grade is calculated on the basis of total soluble solids in the gel, not just the sugar solids.

Table 1 indicates the grades obtained from both jelly strength and sag agree quite closely when the buffer salt solution was used, whereas they do not agree as well in the absence of salt. Without salt, best agreement is found when the slow-set citrus pectin is used. A large portion of the difference in grade is due to the variation of the optimum pH for the particular physical characteristic being measured; these differences in pH are negligible where the synthetic juice mixture is present. Adding the acid before boiling produces the most regular curves whether the salt is present or not. For this reason and because the procedure is more comparable with major factory usage, it would seem to be the one which should be used by the pectin manufacturer for grading. Adding "excess-acid" after boiling, or in the glass, sufficient to adjust the pH to 2.0 to 2.3, produces grades with the highest degree of variance from the factory usage standpoint and should be abandoned.

Conclusions

1. A series of jellies which will produce a jelly strength—pH curve is to be preferred to duplication at one pH, especially at pH values produced by "excess-acid" technique.

2. Synthetic juice buffer salt solutions are of benefit in grading pectins more nearly to the terms of actual usage.

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The Preservers' Stake in Uniform Pectin Grading[a]

E. EVERETT MESCHTER[b] AND LOUIS J. LATAILLADE[c]

The need for uniform grading of pectins is discussed. A method for preparing a standard jelly and physical tests for its evaluation are given. A detailed method suggested by The National Preservers' Association Research and Technical Committee represents an objective approach to the problem of pectin grading.

There are many references in the literature that contain data and present methods and procedures by which pectins can be graded. And yet the preservers, who use more than 70% of the commercial pectin production in this country, have not been heard from. I would like to present the preservers' stake in the controversial issue of pectin grading. Let me, first of all, explain how I happen to speak for the preserve industry on this problem, rather than leave it up to the pectin industry where, perhaps, it rightly belongs.

Early in 1946 the National Preservers Association appointed a Research and Technical Committee whose purpose is to investigate and attempt to solve problems of the industry which are of interest and concern to all members. One such problem, for example—the fading of the rich, red color of strawberry preserves upon room temperature storage—is being investigated under a cooperative research project directed by Dr. Kertesz at the New York State Agricultural Experiment Station at Geneva, N. Y. Another problem under investigation is the fate of DDT spray residues in grapes and grape products. There is no doubt that an attempt to establish a uniform method for grading pectins is within the scope and purpose of this committee and is a problem of importance to every purchaser of commercial pectin. Therefore, we would like to illustrate the need for the establishment of a uniform pectin grading procedure from the preservers' point of view and, suggest a concrete starting point for constructive discussion toward that end.

During the war shortage of pectin the American Preserve Co. was forced to purchase brands and types of pectin which it had never heard of before—and never hopes to again. These pectins were all labelled 100 grade, 150 grade, or some other nondescript value which had meaning only to their manufacturers, but they were so different in their physical characteristics and sugar supporting capacity that it was impossible to substitute one for another in a commercial preserve or jelly batch without considerable adjustment of the formula.

[a] Presented before the Eighth Annual I. F. T. Convention, Philadelphia, Pa., June 8, 1948.

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[c] Tea Garden Products Company, San Francisco, Calif.

On one particular occasion it was found necessary to purchase pectin from an apple processor who had never made pectin before. The actual production of the pectin was of minor consequence compared to the controversy over the determination of the value of the finished product. How would one go about making a "standard" jelly? How would you know it was "standard" once you've made it? There was no legal or scientific basis on which a settlement of grade value could be made. Only the sense of fairness on the part of the contracting parties was able to bring such a difficult situation to a satisfactory settlement. Even today this situation exists. Preserves find certain brands of pectin which, in a given batch, require 10 to 20% more material than other brands of similar stated grade to give equal jelly strength values under identical plant conditions. Instances have been found where a commercial pectin would grade as low as 72% of the jelly strength value of another pectin of the same specified grade.

It certainly seems reasonable to expect any article of commerce as important to another industry as pectin is to the preserve industry, to have a standard of identity by which its value can be graded by the purchaser on the same basis as it was graded by the seller.

The problem of non-uniformity of various brands was presented to the Research and Technical Committee for consideration, and it was decided to determine how wide-spread the difficulty was. A questionnaire was prepared and sent to all members of the Preservers Association. Of the 22 members who had sufficient technical data to return answers, one-third said they used more pectin in their formulas than they did 7 years ago, but apparently this was only the case when using certain brands. It seems that few members evaluate commercial pectins for themselves, most everyone relying on the grade stated by the manufacturers. Members indicated that more information was desired on the pectin which they purchase, particularly as to setting time and grade over a range of acidity common for fruit jelly. The demand for some sort of uniform method of testing and evaluating the pectin was unanimous, and the Committee was thus encouraged to carry the investigation further.

Letters were then written to the pectin manufacturers and the problem explained to them requesting that they make available their standard jelly making technique and method of evaluating the test jellies. It is interesting to note that no two pectin manufacturers used the same method of making a test jelly. No two manufacturers used the same technique on the evaluation of the test jelly, and no two manufacturers used the same method of calculating grade from the observed tests. It is little wonder from this that the preserver finds difficulty in substituting one pectin for another in his formulas.

The Committee has contacted many of the pectin manufacturers and find that they too are anxious to find a standard method for pectin grading. Information on this subject has been collected from many sources and if any of these sources hear their own material being returned to them, then it is freely admitted we are guilty of plagiarism. It is strongly felt that the literature and papers presented here today contain a great deal of valuable information toward uniformity of method, and that the greatest obstacle in uniting them into a standard, accepted procedure is prejudice against competitors' methods or inertia against change of one's own long established practice. So, the method that we would like to suggest today is an attempt to summarize consensus of opinion and consolidate the good points of many of the methods now in use, always bearing in mind, however, that any point chosen is in close agreement with commercial jelly manufacturing practice. It is suggested with the idea that it is a simple, workable and accurate technique, and is presented at this time primarily as a basis for discusion. It is designed for use in grading all types of pectin which are suitable for use in the manufacturing of 65% fruit jellies as defined by the Department of Agriculture for which standards of identity have been established. It does not necessarily apply to the so-called low methoxyl pectins capable of gelation in absence of sugar, nor to pectins which have specific uses in confectionary, leather tanning or pharmaceutical applications.

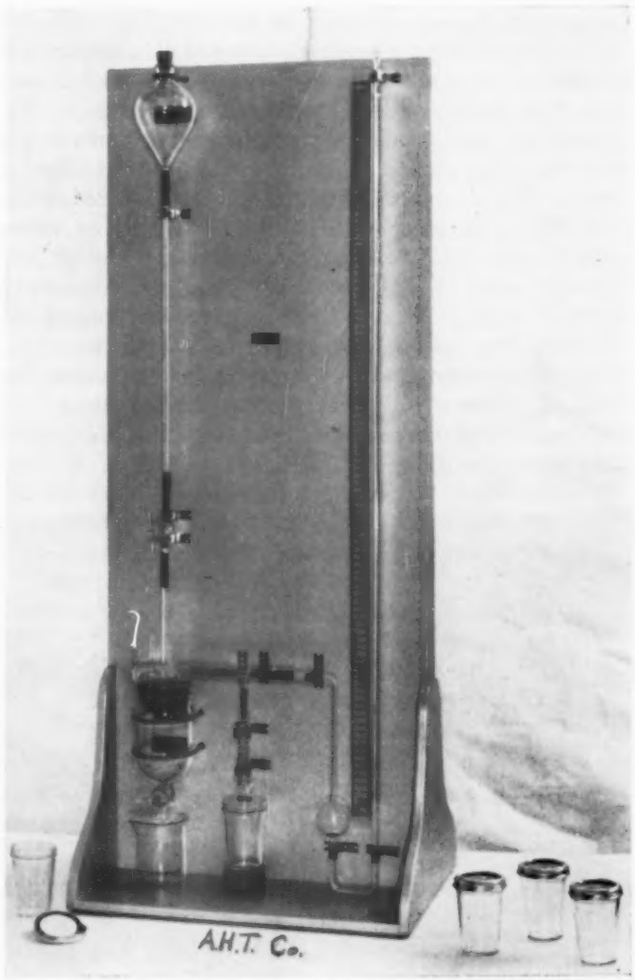

FIG. 1. Tarr-Baker Delaware Jelly Strength Tester. The jelly strength, which is indicated on the water manometer (at right), is determined by measuring the force (air pressure) required to break through the jelly surface under standardized conditions, using a plunger with a flat surface face of controlled diameter (Luer syringe lower center). Air pressure is created by displacement of air in chamber (at lower left) by liquid from reservoir (upper left). (Courtesy Arthur H. Thomas Co.)

This procedure was outlined at a meeting of the Research and Technical Committee several months ago for the purpose of evaluating the present instruments available for pectin jelly testing, and to determine if any one instrument favored any particular type or brand of pectin. The instruments chosen for study were the Tarr-Baker tester, developed at the University of Delaware (Fig. 1); the Ridgelimeter, developed at the California Fruit Growers Exchange (Fig. 2); and the Rigidometer, a development of the Western Regional Research Laboratory (Fig. 3).

The investigation was carried on independently by the authors at the Tea Garden Products Company, San Francisco, California, and at the American Preserve Company, Philadelphia, Pennsylvania. From time to time, the authors collaborated on their findings.

For this study several pectin manufacturers were requested to supply a sample of their standard commercial pectin, which, by their production control methods, was accurately graded. The nine pectins provided, included two slow set citrus pectins, five rapid set citrus pectins and two apple pectins. Then, using the suggested procedure, each pectin was tested and evaluated by these three instruments.

Each pectin was thoroughly dispersed into a solution and made into a jelly in a medium of synthetic strawberry juice proposed by Olsen and his co-workers. In commercial jelly production, pectin is in contact with an acid medium during the entire cooking period. Therefore, in this test procedure, the jelly was boiled with the acid to simulate plant conditions. The jellies were poured into standard ridgelimeter glasses, equipped with sideboards of Minnesota Mining and Manufacturing Company "Wet or Dry" brand masking tape. This tape was preferred over gummed paper tape because it was more easily applied and more easily removed. After three minutes each jelly was skimmed and immediately covered with 2 ccs of paraffin oil. After aging the jellies for 18 to 24 hours at 30° C., the top strengths were measured on the Tarr-Baker tester. The excess jelly was then cut from the top of the glass with a cheese cutter, and modulus in tension was measured on the Rigidometer. Each jelly was then removed from the glass and the modulus in compression was measured on the Ridgelimeter. A third glass of jelly which was not cut by the Rigidometer vane was sliced into seven mm slices for slice strength evaluation on the Tarr-Baker tester. Thus, two measurements of rigidity and two measurements of rupture strength were made on each jelly batch.

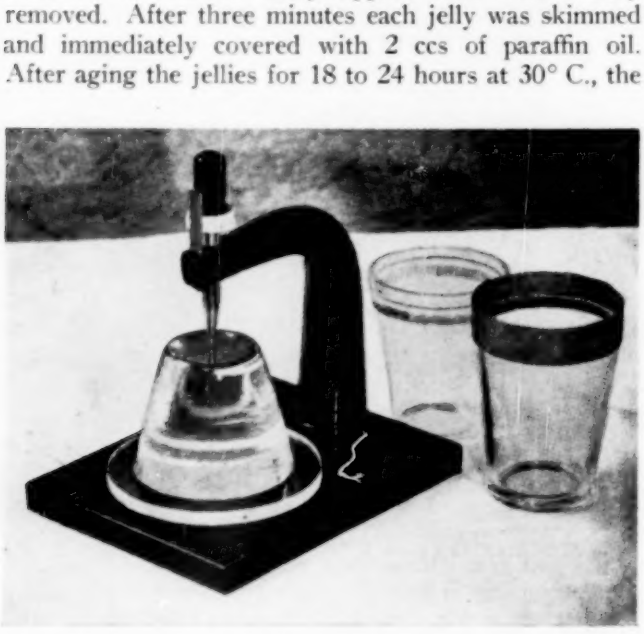

FIG. 2. California Fruit Growers Exchange "Ridgelimeter." Jelly is poured into glass equipped with paper collar or "sideboard" above rim of glass (at right). When jelly is set, "sideboard" is removed and excess jelly cut off with cheese cutter. Jelly is inverted onto glass plate and amount of sag is measured on scale when instrument pointer touches jelly surface.

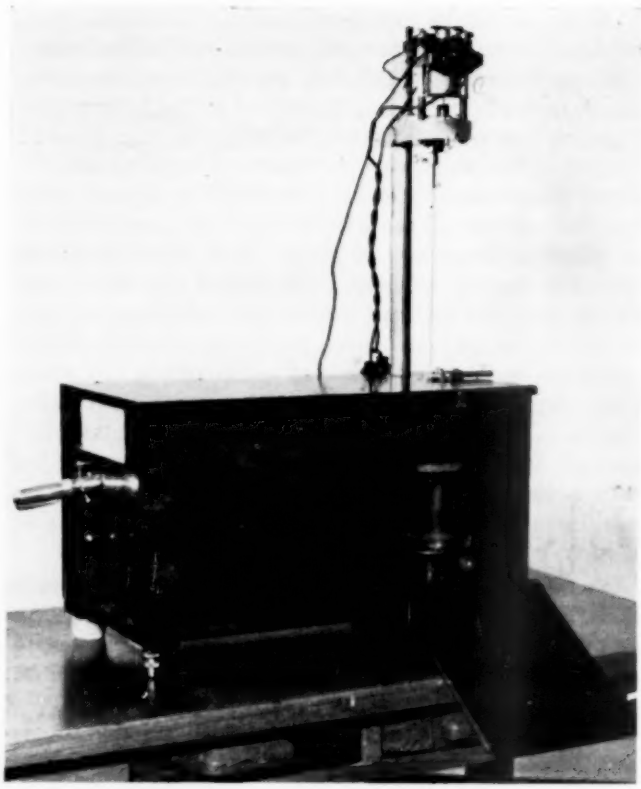

FIG. 3. Western Regional Research Laboratory "Rigidometer." Shear modulus is measured by inserting vane on bottom of wire into jelly (in box) and applying twist of 10° in torsion wire with synchronous motor (upper right). Deflection of vane in jelly is indicated on chart scale (at left end of box) by the reflection of light beam (from light source left center end of box) by mirror attached to upper part of vane.

(Courtesy Western Regional Research Laboratory)

Results of this investigation seemed to indicate the following:

1. There seemed to be a variation of as much as 30% from the highest to the lowest grade of the commercial pectin samples submitted whether evaluated by a strength measurement or a rigidity measurement.

2. There was a close correlation between grades determined by the Exchange Ridgelimeter and the Western Regional Laboratory Rigidometer. They seem to measure identical characteristics of jelly. This is in agreement with the findings of others.

3. There seemed to be a wide variation of grade over the pH range of fruit jelly of 2.8 to 3.4 when grade was determined by either strength or rigidity measurement. This difference in grade over the pH range was greater in some types of pectin than in others.

4. When some pectins were graded over a pH range the rigidity increased with decreasing pH, but the increased rigidity was not necessarily reflected in increased breaking strength and in some instances rigidity increased with decreasing breaking strength, particularly at pH values of 3.2 and below.

5. There appeared to be greater reproducibility of measurements of top strengths of jellies when paraffin oil had been added to the surface, compared to jellies allowed to age covered by a lid. This may be due to the prevention of condensate returning from the lid to the jelly surface.

6. The greatest reproducibility of strength measurement, however, was obtained by the testing of jelly slices.

7. Apparently the rate of pressure increase in the Tarr-Baker tester is extremely important for strength measurements. Variations in grading with this instrument amounted to as high as 15% when rate of pressure increase was changed from 1 cm. of water per second to 3 cms. of water per second.

The original purpose of the investigation was to determine if one particular method of grading favors one type of pectin over another. Apparently it does. Any method of grading based on rigidity appeared to favor most citrus rapid-set pectins, or pectins which tend to be brittle in their character. A rigidity evaluation tends to lower the grade of most apple pectins because of their greater elasticity. However, increased rigidity is not necessarily reflected in increased breaking strength. Therefore, it does not seem possible to assign a fair grade to all pectins on the basis of a rigidity measurement alone. The inference is not that pectins graded by a rigidity measurement are not fairly graded. Preservers of this country have been too well satisfied with the quality and uniformity of their results with these pectins to criticize this method for production control. But the average preserver does feel that a pectin graded by a rigidity method has been satisfactory because at a particular standard percentage of sag the breaking strength has also been satisfactory, and not primarily because the attributes of jelly of standard sag-value contributes greatly to desirable qualities of that jelly.

One may well say, "let's grade apple pectins on breaking strengths and citrus pectins on rigidity." Unfortunately, mixtures of several types of orange, lemon or grapefruit pectins yield various characteristics of sag in relation to their breaking strength. And there can be no sharp line of demarkation between a so-called elastic jelly and a rigid jelly.

Preservers are primarily interested in breaking strengths. This characteristic determines whether or not a jelly will retain its mold on pouring from a container, whether or not it will stand abuse in shipping and, most important, how the jelly will react on a piece of buttered bread when spread with a knife. A rigidity measurement gives valuable descriptive information, but jelly quality can be considered satisfactory over a wide range of rigidity. Jelly quality can not be considered satisfactory over such a wide range of breaking strength. Perhaps the *relation* of rigidity to breaking strength may be an important criterion by which jelly character can be described. If pectin were graded on rigidity alone, then a preserver could conceivably receive pectin which yields a brittle agar type of jelly which would be entirely unsatisfactory for commercial fruit jelly. If graded on breaking strength alone, the preserver could conceivably be supplied with pectin which yields jelly of satisfactory breaking strength and yet be so elastic as not to form a shimmering mold of the container when poured out for table use.

It would, therefore, seem necessary to grade all pectin on the measurement of *both* breaking strength and rigidity. Pectins are all different. We must stop talking about pectin and start talking about pectins. The steel industry has specifications for tensile strength, rigidity, elasticity and malleability. Each steel has advantages for a particular purpose. This is also true of pectins. We can not expect one measurement to completely describe pectin characteristics any more than we can expect tensile strength alone to tell an engineer the adaptability of a given steel for a bridge span or a structural support. Likewise, values of breaking strength and rigidity of pectin jellies describe different characteristics of these jellies, and increase our knowledge of the adaptability of a pectin for a particular use.

Preservers are interested in the evaluation of pectin jelly quality in their every-day production. It would seem reasonable then that any instruments used for grading evaluation should also be capable of telling results of pectin usage under commercial production conditions. This is the only way that a preserver could tell if commercial production reflects the value of the stated grade.

For the measurement of breaking strength, our investigation has shown that greatest reproducibility is obtained by the use of jelly slices. This technique has the decided advantage to preservers that the area of the container from which the sample was taken is of no significance. Consequently, uniform results can be obtained on jelly slices from 6 oz. glasses or 30 lb. pails (Fig. 4). The principle of the Tarr-Baker tester can

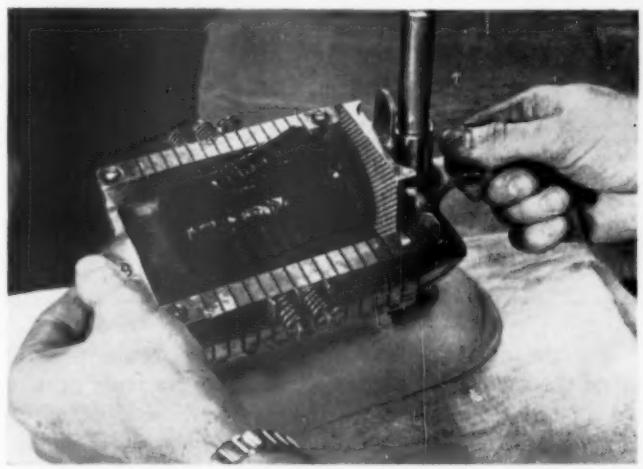

FIG. 4. Jelly slicer designed to cut slices of uniform thickness from portions of jelly from any size container. An adaptation of a butter cutter, the blades are .006 in. machinist feeler gauge stock under spring tension 7 mm. apart.

probably be developed to measure breaking strength with satisfactory accuracy. Particular attention must be paid to the rate of pressure increase, maintenance of clean plunger and barrel surfaces, and evenness of slices used for measurement. Perhaps many of these difficulties could be overcome with the development of a mechanical instrument similar to the one developed during this investigation. This mechanism is presented for consideration since we believe it may eliminate much of the difficulty in breaking strength measurements. It is not new, but merely a modification of Stoloff's device used for surface strengths. Stoloff placed the jelly sample on a dietary scale and read from the dial the pressure necesary for a plunger to break through the jelly surface. To this device we have added a constant speed motor driving the standard Tarr-Baker plunger head. The test jelly is placed on the pan of a tare beam balance. The motor drive is supported over the jelly and the plunger driven into the sample at a constant speed. The pressure increase on the jelly is reflected directly on the deflection of the scale pointer. Break-through is sharply indicated by a drop in the scale pointer. The rate of pressure increase is constant. Friction is not a factor since the balance pan is supported on knife edges. Results can be reported directly in grams per square centimeter of plunger area. The mechanism can be constructed for less than $100 in any machine shop from simple specifications and needs no arbitrary standardization since it is purely mechanical and measures directly in units of force (Figs. 5 and 6). For convenience we have called it the "Stolmotor" device.

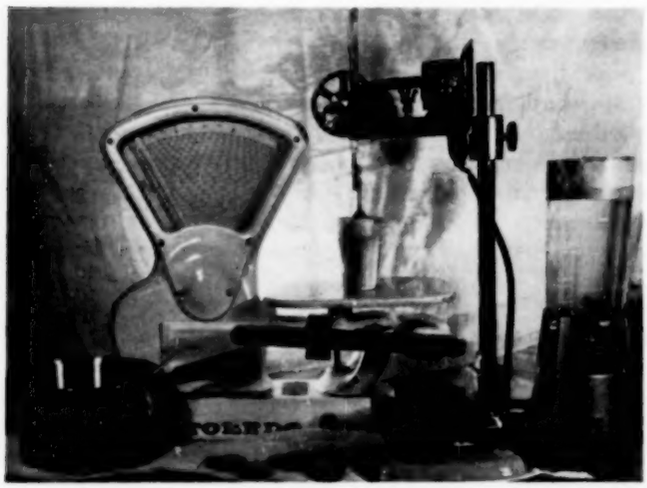

FIG. 5. Equipment suggested for jelly strength evaluation. From left to right: 4 quart Stainless steel saucepan with stirrer, tare beam balance, "Stolmotor" device, jelly slicer, and Waring Blendor.

For the measurement of rigidity we would recommend the use of an instrument based on the same principle as the Rigidometer. From a preservers' point of view this principle has an advantage over the Ridgelimeter because it can be redesigned to make a rigidity measurement on jelly in any package of any shape. It has already been shown to compare favorably in accuracy and characteristic of measurement with the Ridgelimeter, and would seem to afford a convenient means of determining rigidity.

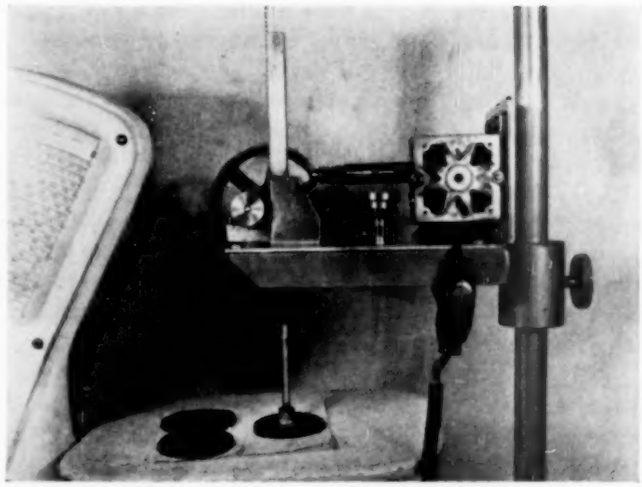

FIG. 6. "Stolmotor" device developed during the investigation. Essentially a constant speed motor with speed reduction to drive standard Tarr-Baker Tester plunger head into jelly at rate of 11 mm. per minute. Breaking strength of jelly is indicated by a sharp drop in scale pointer (left). Highest weight reached is reported as breaking strength.

It is not likely that any definite decisions can be made at a meeting of this size. We appreciate the cooperation of the pectin manufacturers in attending this meeting so that all phases of the problem can be openly discussed. It is impossible to evaluate information and ideas of other workers which will be presented at the meeting today without an opportunity of trying them out for yourselves. We, therefore, suggest that this afternoon a committee be formed to investigate and formulate a uniform jelly-making method, a uniform jelly-testing procedure, and a uniform grade-calculating formula by which all pectins suitable for 65% fruit jelly shall be graded.

We suggest that this Committee be composed of several representatives from pectin manufacturers and several representatives from the National Preservers Association. In such a group all factions interested in this problem would be represented and we feel confident that a method can be worked out by which all pectins can be fairly and accurately graded.

. . . .

METHOD FOR GRADING PECTIN

(Suggested by National Preservers Association Research and Technical Committee)

Equipment:

1. Waring Blendor with 1 liter glass cup and stainless steel blades, equipped with rheostat. This equipment has a universal motor. (The speed is proportional to the voltage.)
2. Four-quart copper bottomed stainless steel sauce pan with 1 side handle. (We found Thermic Ray made by Norris in San Francisco to be very good. Revere does not make a 4-quart with a single side handle.)
3. 50% Citric Acid Solution
   Dissolve 500 grams anhydrous U. S. P. citric acid in distilled water in a 1 liter volumetric flask. Make up to mark. This solution contains 50 grams anhydrous citric acid in 100 cc. solution.

4. Olsen Salt Solution—modified to contain 47.3 grams citric acid instead of 62.3 grams. The final pH of this solution is then 3.4 and attains the correct pH of the first jelly without further adjustment. pH of subsequent jellies can be adjusted by addition of further acid solution.

FORMULA FOR CONCENTRATED SYNTHETIC STRAWBERRY JUICE
(Olsen's Salt Solution)

Ingredient	Formula	Amount 1 kg.
		grams
Distilled Water	H_2O	800.0
Sodium Salicylate	$NaC_7H_5O_3$	0.32
Salicylic Acid	$C_7H_6O_3$	0.21
Potassium Phosphate	K_3PO_4	3.83
Potassium Citrate	$K_3(C_6H_5O_7) \cdot H_2O$	15.7
Sodium Citrate	$Na_3(C_6H_5O_7) \cdot 2H_2O$	2.03
Citric Acid, Anhydrous	$H_3(C_6H_5O_7)$	47.3
Magnesium Acetate	$Mg(C_2H_3O_2) \cdot XH_2O$	5.07
Calcium Citrate	$Ca_3(C_6H_5O_7)_2 \cdot 4H_2O$	3.80
Distilled Water	H_2O	q. s.
	Total Weight	1000.00

Add ingredients in the order given, or if already weighed out for use, add as a mixture. Make up to 1000 grams with distilled water and stir mechanically until dissolved. Use 134 grams per batch of jelly of 1000 grams. Keep juice in a well corked bottle since exposure to air has some effect in causing precipitation of salts.

The Salicylic Acid and Sodium Salicylate are added to prevent mold.

5. Gas burner or electric hotplate—adjusted to boil off water from 1000 gram batch at rate of 100 grams between 2 and 3 minutes.
6. Stirring rod—tared with pan.
7. Hazel Atlas tumblers No. 85 (used as standard Ridgelimeter glass by California Fruit Growers Exchange) equipped with "Sideboards" of Minnesota Mining and Manufacturing Company 1½" "Wet or Dry" Masking Tape.
8. Spatula with sharpened edge to cut 7 mm. slices of jelly.

Procedure:

1. Determine approximate grade:
   Make a 1% solution of pectin and determine its viscosity. Calculate approximate grade by formula

   $\text{Log } y = ax + .2$ where

   y = relative viscosity at 26° C.

   x = grade or sugar supporting capacity of a unit weight of pectin

   a = variable factor (.6 for citrus pectins, .7 for apple pectins)

2. Prepare a pectin solution containing 3250 jelly units in 1,000 grams

   For 5 grade liquid pectin: Dilute 650 grams of concentrate to 1000 grams with distilled water.

   For powdered pectin: Weigh out an amount of pectin determined by dividing 3250 by the assumed grade of the pectin. (For 150 grade use 21.66 grams, for 100 grade use 32.50 grams.)

3. Make certain of complete solution of pectin.

   A. Place approximately 800 grams of distilled water @ 50° to 60° C. in tared Waring Blendor cup. Adjust rheostat to low motor speed and cautiously add the 3250 jelly units of dry pectin to the mixing cup. Allow to run for two minutes, gradually increasing speed of Blendor as viscosity of solution increases.

   B. After running three minutes or until pectin particles are no longer visible, return the Blendor cup to the scale and add distilled water to a final solution weight of 1000 grams. Return the cup to the Blendor and mix thoroughly at a speed as great as possible without loss over sides of cup.

   C. This solution is such that 650 jelly units are contained in 200 grams of solution.

4. Preparation of Jelly:

   A. Prepare 4 jelly batches—at pH 3.4, 3.2, 3.0 and 2.8.

   B. Weigh out 650 grams of sugar for each batch, subtracting from the sugar weight the grams of other solids to be added to the batch.

      1. Use the apparent refractive sugar solids of the salt solution as 7 grams solids.
      2. Each cc. of acid solution contains ½ gram anhydrous acid.
      3. Pectin contained in the 200 grams of solution equals the weight of weighed pectin sample divided by 5.

   C. Place the tared stainless saucepan on the balance. Weigh out 200 grams of pectin solution. Add 134 grams of Olsen's modified salt solution. (Omit salt solution when testing liquid apple pectin concentrates). Add sufficient acid solution to adjust the pH to the desired value (jelly pH 3.4 equals 0 acid; 3.2 equals 4 cc. acid; 3.0 equals 10 cc. acid; 2.8 equals 20 cc. acid). Add sufficient water to bring the total weight to 1100 grams minus weight of sugar to be added.

   D. Place pan with liquid ingredients on burner adjusted as in paragraph 5 under "Equipment." Stir occasionally to prevent burning. When boiling commences, add the sugar. Stir constantly until all sugar is dissolved. Boil until weight is reduced to 1000 grams. Pour into glasses described in paragraph 7 under "Equipment." Allow to stand for 3 minutes and skim. Immediately add 2 cc. paraffin oil to surface.

5. Measurement:

   A. Age jellies for 18 to 20 hours @ 30° C.

   B. Remove sideboards and slice off excess jelly with wire cheese cutter. Measure shear modulus on two glasses with instrument similar in principle to Rigidometer. Measure breaking strength on 7 mm. slices cut from third glass on instrument similar in principle to Tarr-Baker tester.

   C. A standard jelly has a shear modulus of 3 grams per sq. cm., and a slice breaking strength of 60.7 grams per sq. cm. of plunger area.

The Need for Standardization of Pectin[a]

H. H. MOTTERN

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REVIEW PAPER

Some of the physical and chemical variations of pectin are described. The need for practical tests and some of the instruments for making them are discussed.

Nature has imposed a wide variation in the raw materials used by the food manufacturer. This makes the standardization of these products difficult, yet it is necessary to standardize in order to assure a uniform final product.

We have seen commercial pectin improve from the cloudy, dark solution of the first manufacturer, Douglas, containing a greater percentage of impurities than of pectin itself, to the present highly refined product meeting National Formulary standards. At the same time the use of pectin has emerged from an adulterant to conceal the inferiority of less fruit ingredient to a recognized ingredient necessary to obtain a satisfactory quality in jellies.

Perhaps the first significant effort toward development of standards for pectin for food use came with the heavy purchases for Lend-Lease purposes at the beginning of World War II. The quantity involved was approximately equal to production at the time. There was much speculation as to what it was actually being used for. One idea was that it was being nitrated to form an explosive for use in detonating block-busters. Another theory (this one facetious) was that it was to be used to jell the surface of the English Channel so that the invasion forces could march across. The quantity appeared quite sufficient! Seriously, England had been forced to reduce the fruit content of preserves and needed the pectin to make up the deficiency in the wartime substitute. Also, at the then current rate of sinkings, in order to guarantee delivery, about twice the quantity had to be shipped.

In obtaining samples and quotations on the pectin which various manufacturers would supply, the wide variations both in grade and purity, became apparent. Since British preservers would be receiving products of various manufacturers without direct contact with the source, it was necessary to develop a standard test for grade.

Early in 1942 tentative specifications were prepared, and submitted to various interested parties for comment. Reviewers in general stated the proposed specifications were "all right, BUT . . . ," the coments were more lengthy than the specifications!

Now we can possibly agree, here among ourselves, that pectin should be standardized, and then spend the rest of the afternoon arguing on the method to be used, only to conclude that because of this lack of a method acceptable to our various ideas we should not attempt to set a standard.

Standardization leads to stabilization and too often this leads to stagnation. Pectin technology is a growing field of science and I would not want to see it stagnated, but I believe we have arrived at the point to consider whether or not pectin should be standardized for jelly manufacture.

A few years ago a representative of a pectin manufacturer made the statement that pectin should not be standardized as variation in grade was the only means of competing since the price was already pretty well standardized. This manufacturer would not have been willing to accept scrip instead of U. S. Treasury notes in payment for pectin as a means of the preserver meeting competition. If we can accept the principle of standardization then we are a step toward the details.

Now pectin varies in many ways. It is not a definite chemical entity, but any preparation represents a mixture of more or less related compounds. Of first consideration is molecular size. Any representation of this property is a statistical average. The true molecular weights of the individual molecules present in a given preparation may spread over a wide or over a narrow range. It may have a large proportion near the average or an even distribution throughout. In referring to the molecular weight of pectin it is necessary to keep in mind how it was determined and whether the numerical average or the weight average was determined by the particular method of measurement employed.

Similarly, any representation of the degree of esterification is an average value. Distribution in the degree of esterification can also vary from molecules resembling pectic acid to highly methylated molecules. There is another type of distribution possible with esterification and that is within the molecule itself. The ester groups may be scattered on alternate carboxyls or grouped at one end of the molecule with a marked effect on chemical properties. In addition, there are impurities and perhaps added ingredients. However, it is not so much these specific differences with which we are concerned in standardizing pectin as it is their outward manifestations on the properties of gel strength, setting time, and solubility.

Much diversity of opinion exists in regard to method of measurement of gel strength, first as to the method of preparation of the test gel and then, the method of testing the strength of the gel. Most directions read as if they were taken from a cook book. Certainly the use of laboratory equipment instead of pans and spoons, gets away from the kitchen methods used in the past.

The question of the pH value at which test jellies shall be made requires discussion. First let it be known that the grade as stated does not necessarily mean that a preserver is going to use it at that ratio to sugar in his product. He may derive more or less jellying power from the fruit used and the pectin is added to correct the deficiency. Furthermore, he may want a tender jelly for local consumption and a tougher jelly for distant shipment. The pH of the jelly will vary with dif-

[a] Presented before the Eighth Annual I. F. T. Convention, Philadelphia, Pa., June 8, 1948.

ferent fruits and this will affect the strength of jellies obtained with the same amount of pectin and with different pectin preparations.

If we are to standardize pectin we must agree on a pH for test purposes realizing it may not be used at this pH, and that the pH at which it is used may affect the strength of the jelly. The pH should be close to that of most common jellies. If we have a pectin standardized at a certain pH then we can better correct for the factor of a different pH in the jelly. Opposition to use of a stated pH in jellies in favor of the optimun pH might just as well follow an analogous line of reasoning and conclude that pectin cannot be standardized, because the fruit juices in which they are used contain a varying amount of pectin, rendering such standardization impossible. Let the preserver know what he is buying and he will be in better position to make suitable corrections in formulation. Whether or not a stated concentration of salts should be used in test jellies is debatable.

The method of testing the strength of the test jelly will receive much discussion. There are old-timers with an educated little finger who will want to continue to rely on it. The finger test is fairly reliable with an experienced person when comparison is made with standard jellies. The inexperienced do not trust it. Moreover, it does not give an accurate estimate of the degree of variation from a standard jelly.

The Tarr-Baker or Delaware jelly tester has been used perhaps more than any other instrument for testing jelly strength. The criticism has been made that the apparatus has not been standardized and that one does not get readings in C. G. S. units. It is a relatively simple process to calibrate a given Delaware tester from the ratio of the diameter of the head of the plunger to the diameter of the plunger itself, taking into consideration the weight of the plunger. A calibration chart can be made using standard pectin. By reduction to C. G. S. units, a standard pectin would not need to be used but it would be necessary to agree to the pressure representing 100 grade pectin under standard conditions of making the test jelly. Using standard 100 grade pectin as agreed upon by suppliers under Lend-Lease we found the instrument in use at Eastern Regional Research Laboratory to give us a reading equivalent to 93 g. per square cm. for a standard jelly.

The Bloom jelometer has been used for some time by the gelatin and glue industry. It is a more standardized instrument than the Delaware testes, being constructed to rather rigid specifications rather than assembled from available parts. This equipment has not heretofore been available to preservers because of limitation on its sale to the gelatin industry only, but it is now offered to preservers as well. It has not been generally studied by pectin people except those who are also interested in gelatin. It is worthy of consideration along with other jelly testing equipment.

Another instrument which has been suggested is the California Fruit Growers Exchange "Ridgelimeter." This equipment measures the per cent sag in a jelly and will therefore give a reading less favorable to a jelly with a high elastic modulus than one with a low elastic modulus.

The British have made use of the B. A. R. tester. B. A. R. stands for the British Association of Research for Cocoa, Sugar Confectionery and Jam Trades, London. This measures the torque on a blade immersed in the jelly produced by a weight and is another means of measuring elastic modulus.

Recently, Owens, Porter and McClay *(1)* of the Western Regional Research Laboratory have developed a device along the lines of the B. A. R. tester which measures shear modulus. Cheftel and Mocquard *(2)* have also designed an apparatus along similar principles which measures elastic modulus. Another instrument has been developed in Kodak Research Laboratories by Goldberg and Sandvik *(3)*. This measures elastic constants by oscillating at frequencies of 10 to 6000 cycles per second. A modification allows measurements of shear which are recorded photographically.

We should decide which property we are most interested in measuring, shear or elastic modulus, or both, and select an instrument which is best suited for measuring this property. In measuring the quality of a fruit jelly we are perhaps most interested in shear. The instrument selected must not be unduly complicated, but rapidly adapted for routine use for control purpose. For research, especially with low-ester pectin gels, we certainly will need to use instruments measuring both shear and elastic modulus.

Since pectins lose grade on storage we should buy on the basis of grade for current deliveries but not be disappointed if we find some months later it does not conform to grade. We will also want to consider standards for color, clarity and solubility.

Because of the many diverse lines of specialized uses we are not ready for standardization of pectin for food use other than by preservers.

It is not within our province to consider standardization of pectin for pharmaceutical purposes but mention should be made that pharmaceutical pectin is a standardized product meeting specifications stated in the Eighth Edition of the National Formulary.

Low-ester pectins are new products and have not yet developed to the point where stabilization by standardization is considered desirable.

Grade Standards have been developed by the Agricultural Marketing Service for such ill-definable products as a number of fresh fruits and vegetables both for the fresh market and for processing. An exception is the cider apple—no one is willing to define it on paper. For the past two months the Food and Drug Administration has been conducting hearings with a view toward defining standards for certain frozen fruits. It is estimated that with the different varieties and various methods of packing over 300 products are under consideration. Surely we food technologists can determine and agree to standards for preserver's pectin.

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Notes and Letters

Survey of Food and Nutrition Research[a]

(Condensed)

In 1946, upon request of the Quartermaster Food and Container Institute for the Armed Forces, the National Research Council undertook to design and effectuate a nationwide survey of active research in the fields of foods and nutrition. The objectives of the survey were to be as follows:

(1) The determination of the major food research problems in the United States, particularly those of definite significance to the national welfare.

(2) A listing of facilities available for food research and development.

(3) An estimate of the extent of food research and a characterization of the subject matter covered.

(4) An evaluation of the adequacy of coverage in the various fields of food research.

(5) An evaluation of the adequacy of educational programs pointed to the training of food research personnel, both at undergraduate and graduate levels.

It was envisioned that the attainment of these objectives would not only serve the interests of national security but would also serve as a convenient basis for coordination of research and guidance for all concerned with foods and nutrition.

The task of implementing the survey was assigned to a committee of the Food and Nutrition Board which operates within the Division of Biology and Agriculture of the National Research Council. The committee was constituted of Dr. C. G. King, chairman; Dr. Floyd Daft, Dr. C. A. Elvehjem, Dr. H. E. Longenecker, Dr. L. A. Maynard, Dr. H. E. Robinson, and Dr. Louise Stanley. Mrs. Mildred Ragan was engaged as technical secretary for the committee.

As the first step, a listing of academic, industrial, and governmental laboratories engaged in food and nutrition research was compiled, and this was extended to include those who financed research outside their own organization. This resulted in a compilation of 522 universities or colleges, 1,005 industries, or trade associations, and 119 foundations, public trust funds, or research institutes concerned with food and nutrition research.

In August 1947 and in subsequent appeals the directors or heads of these laboratories were requested to furnish the following information:

(1) A list by subject of research projects pertaining to foods and nutrition currently active in or being supported by their organizations.

(2) A list of professional personnel responsible for conducting or directing the research listed.

Definition of the information desired was not explicit except to indicate that all phases of food and nutrition research were to be considered including chemical, physiological, technological, microbiological, and basic economic studies. Concepts as to the scope and nature of research vary widely. The committee felt it was better to allow those from whom the information was solicited to formulate the returns in accordance with their own understanding. In this way it was anticipated that limiting patterns and definitions would more or less establish themselves.

There were some misgivings, particularly among the larger industries, as to the intent and purpose of the survey. Also some difficulties were encountered in attempting to distinguish between so-called basic and developmental research. No clear-cut distinction can be made in this respect, and it was left to the judgment of those submitting the information as to what limitations should be applied. Likewise, some were reluctant to list their professional research personnel without a clearer indication of what kind of personnel list was to be drawn.

In spite of these and many other problems which came up while the information was filtering in, it is believed that a major portion of food and nutrition research active during 1947 has been recorded in this survey. In the 306-page compilation, published by the Food and Nutrition Board of the National Research Council, there are listed by subject over 4,000 projects in food and nutrition research. These were submitted from over 600 organizations. Of this number of organizations, 39 percent were classified as academic, 14 percent were classified as governmental, and 47 percent as industrial. The number of investigators listed approximates 5,000.

The initial report has been divided into four sections. The first section includes the list of numbered research projects classified by subject and referred to the appropriate conducting or supporting organization by number. The second section is an alphabetical list of organizations conducting or supporting food and nutrition research. Each organization is given a numerical code number to which the projects and personnel are referred. The third section is an alphabetical list of research personnel responsible for the conducting or direction of the research. The highest academic degree is included, and each investigator is referred to his organization by the assigned code number. The fourth section is a comprehensive index of the subject material referring to the projects by number.

In order to indicate the relative distribution of projects, the projects assigned to the field of physiology represented 40 percent of the total, projects involving primarily food chemistry made up 30 percent of the total, projects of food technology 15 percent, economics 9 percent, microbiology about 5 percent, and psychological studies numbered less than 1 percent of the total.

[a] Presented before the Eighth Annual Institute of Food Technologists Convention, Philadelphia, Pa., June 7, 1948.

This survey could probably be more properly designated as a comprehensive compilation or registry of food and nutrition research. It is hoped to keep the registry continuous and up to date. Appreciation is due those who have provided the information, and continuous cooperation is requested. There were unquestionably unfortunate omissions which it is hoped will be corrected. Copies of the published report and further information can be obtained from the Food and Nutrition Board, 2101 Constitution Avenue, Washington, D. C.

LeRoy Voris

Executive Secretary, Food and Nutrition Board, National Research Council, Washington, D. C.

Position of Food Technologists in National Emergency[a]

(Condensed)

That we were unable to strike back at the outset of World War II is a matter of record. Of particular concern to us was the relative unpreparedness of the food industries and of technologists, as a group, when the first blow was struck. What was wrong with the use we made of food technologists during the recent war? We have come a long way from the "Corn Willie and hard tack" diet of World War I. World War II moved us forward to such notable developments as rations with greatly increased variety of meat products, improved nutritive value, and greater stability in storage.

So much for the black side of the ledger; the red side is somewhat disturbing. Although industry, in peacetime, may have felt itself adequately supplied with food technologists, the special feeding requirements created by the national emergency staggered the industry with demands that could not be met adequately with the technologists available. These shortages of personnel were, of course, aggravated by the tremendous demands of selective service.

Another debit item, which in reality antedated the war, was the lack of a technological training program. Had systematic training programs been in operation, the nation could have adjusted itself to war much more rapidly.

But of all the items in the debit column, the most serious was the lack of proper utilization of our technologists by the Armed Forces. The report of the AD HOC Research and Development Advisory Committee of the Reserve Officers, dated March, 1948, presents some depressing facts. Out of a representative group of 100 technologists in uniform, the talents and skills of only 30 were fully utilized. The services and skills of 33 were utilized for only half of their period of military service. Out of the remaining 37, little or no use whatsoever was made of their technological education and experience. Such wastage is downright dangerous. Since the next war will be far more technological than the last, we must not let this happen again.

Guided missiles, armed supersonic planes, radioactive dust, or diabolical weapons could strike tonight.

Whenever they strike, however, tonight or in the future, we can anticipate two immediate problems—the serious disruption of normal food channels, and the total destruction of segments of our food manufacturing structure. As food technologists, we will be engaged in rehabilitating destroyed food facilities and in restoring normal food channels. We shall also have the *primary* responsibility of food research and development.

The problem of the food technologists will suddenly become two-fold:

(1) to insure adequate feeding of the domestic civilian population, and

(2) to provide rations for the armed services at home and overseas.

Let no one underestimate the complexities of the global feeding problem of the next emergency. The power of offense has been increased and warfare will be open and characterized by rapid movement. Airborne operations in a future war will probably be on a scope and magnitude not conceived of today. Many people, today, think war will be fought in all parts of the world with the likelihood that an important locus of operations will be the polar region. The implications are many. As for food, ration research and development must be pursued with renewed intensity, with particular emphasis on stability, acceptability, and nutrition. The rations must be compact, light in weight, adaptable to special environmental conditions, and easily prepared.

Added to these complexities is the need to adjust rations to the physiological and psychological requirements of soldiers under environmental and emotional stress. There will, of course, be many other problems.

After hostilities have once begun there will be little or no time for planning. The optimum moment for organizing our personnel and resources for total preparedness is now. We must think in terms of what will be expected of the food technologists in the next emergency. Further, there should be placed in the hands of the technologist a plan sufficiently detailed to indicate his individual responsibility.

The Department of the Army has drafted and approved an initial plan for the training and mobilization of scientific personnel who are Reserve Officers (per ltr OQMG 28 May 48) in a national emergency.

The objectives of the plan are:

a. To establish a program for Reserve Officers who are professionally engaged in research or development which will—

(1) Maintain the useful affiliation of this type of personnel with the Organized Reserve Corps.

(2) Provide peacetime assignment for these officers, enabling optimum utilization of their education, experience, and skills.

[a] Presented before the Eighth Annual Institute of Food Technologists Convention, Philadelphia, Pa., June 7, 1948.

(3) Furnish mobilization assignments which will fully utilize their talents.

(4) Adequately prepare these officers for mobilization.

b. To establish adequate means for the selection of Reserve Officers of this category to participate in this program.

The plan itself calls for an organization in each military district where there are a sufficient number of reserve officers who are professionally engaged in research and development. For example, the technologists of the Philadelphia area under this plan may be organized into a Reserve Research and Development Group, provided a minimum of 20 officers indicate their desire to be so organized. Where fewer than 20 reserve officers are available, sub-groups may be organized.

The final selection of qualified reserve officers for participation in this program will be made by the Department of the Army. In order to be eligible for selection, reserve officers must have the following qualifications:

(1) Possess at least a Bachelor's Degree, from a college or university accredited by one or more of the recognized national or regional educational accrediting associations.

(2) Be engaged in a professional capacity in research and/or development work in a field normally associated with one of the physical, engineering, medical, or biological sciences, including pertinent fields of psychology.

Professional employment in a field or activities more properly associated with routine or maintenance functions will not necessarily be considered as professionally qualifying an officer to participate in this program.

These requirements may be waived by the Department of the Army if the applicant's professional background and experience so warrant.

In peacetime, reserve officers will be given inactive duty assignments by the Department of the Army to Organized Reserve Research and Development Groups or sub-groups for training. Inactive duty training will have the following scope:

(1) Orientation on the organization of research and development activities of the Department of the Army, of the Army Field Forces, and of the various technical services, including those boards and panels whose functions fall within the purview of research and development.

(2) Pertinent parts of courses from established schools and colleges of the armed forces.

(3) Review and editing of technical manuals and publications.

(4) Work on certain research and development material and non-material problems as assigned by the head of the appropriate technical service in coordination with Research and Development Group, Logistics Division, General Staff, United States Army.

(5) Review or formulation of plans to assist research and development organizations, boards, or panels in accomplishment of their mission.

(6) Review or formulation of planning methods or the evaluation of proposed tactics, technics, and organization.

(7) Assistance to service schools in revising or broadening their training programs.

(8) In view of the technical qualifications of the Reserve Officers participating in this program, they will be encouraged to formulate their own training programs encompassing research and development problems or projects of interest to the Department of the Army.

Active duty training will be subject to the availability of funds. Reserve Officers assigned to Organized Reserve Research and Development Groups or Subgroups, may be assigned to research and development agencies, schools, and boards of the Department of the Army, the Army Field Forces, area commands, or the various technical services for active duty training upon request.

In time of war, assignments will be made to appropriate Research and Development installations or offices. These assignments will be made by the Department of the Army. Each assignment will be subject to review at any time to determine that the officer concerned is the best officer available.

That is the essence of the plan.

Col. C. S. Lawrence
President of the Quartermaster Board,
Camp Lee, Virginia

Neglected Aspects of Food Technology

All food technologists should aspire to be broad-gauged, fully-rounded members of the profession. It is imperative that all members of I. F. T., especially those of us who have left the institutions of learning and are now in industry, should endeavor to develop themselves to that end.

Nevertheless, one need only look at the programs of our meetings and the contents of our journal to observe the tendency of our interest to center around the preservation of fruits and vegetables. Which is not to object to this important interest but to point out that there is far more to food technology than the mere preservation of certain perishable foods by heat sterilization or freezing. We are decidedly lop-sided in our interests at present.

Those who have reached mature years in food technology are not looking for rapid transition from a narrow or highly specialized view of the profession, but they have a right to look for important nearby moves in the direction of broad fundamental training for those about to enter our ranks. It is our duty to encourage—or even insist—on adequate training for the coming generation of food technologists.

Is not the production of milled cereals within our field? Is not the production of bakery goods a part of food technology? How about dairy products of all sorts? Confectionery? Malt beverages? Carbonated beverages? Shortenings? Bread spreads?

Or, instead of considering the field, product by product, how do we stand on functional concepts? We are strong on science, especially chemistry, biochemistry, bacteriology and nutrition; we are strong on sanitation and certain aspects of heat application; we are fairly good on control of the oxidative deterioration of fats, also on quality control—to mention a few of our better points.

But we are weak on many other important matters. For example, we are weak on management, administration, plant layout, process engineering, packaging and materials handling. The latter pair are definitely within the province of food technology, although the matter of plant layout and process engineering is regarded by some of our best known food technologists as outside our scope. To the extent that industry does not need to turn to the food technologist for solution of such problems, the opposition view is undoubtedly right. There can, however, be no debate on the need to include packaging and materials handling in food technology. Too often the food technologist is lacking in a fundamental understanding of this inseparable pair of functions, yet he is under a definite obligation to include them in his professional equipment.

Perhaps there is an historic reason for the neglect of packaging and materials handling by the majority of those who now constitute our membership. Heat sterilization of foods requires the use of a rigid container—the tin can or the glass jar. Such containers happen to be the most durable consumer packages that exist, especially the tin can. Since food technology has achieved recognition more rapidly in the field that uses the tin can or glass jar than in any other, we are wont to accept the rigid container without realizing that it is a package. And certainly we accept it without realizing that among all types of packages these two types of rigid containers occupy a special—almost unique—position. They are very "long-lived" packages, and they provide more nearly complete protection than any other conventional package.

A further influence on our acceptance of rigid containers without conscious realization of their packaging function is the fact that the makers—not the users—of these containers always decide what gauge of steel, what weight of tin plate, what lacquer or enamel is appropriate for tin cans or for metal closures that a customer may need. The food technologist of the packer's organization does not specify these things very often. Usually he or his company receives them without knowing that the technical decisions have been made on his behalf by the container manufacturer.

What a contrast to the problem of the food technologist in dealing with flexible containers! Here he is largely on his own. He alone must decide what materials are needed or are satisfactory to package his product.

In all types of food the proper packaging is for a definite period of time, the length of which is determined by many factors such as: the characteristics of the food, the climate in which it is to be distributed and consumed, the sales and distribution policies of the food company, the sanitary environment to be withstood, the rapidity of turnover, and so on. The period may vary from a few days to a matter of a few years. It is a finite time. One does not package for eternity—it costs too much, even if it were technically possible.

Decisions on the preceding matters are usually executive decisions concerning which the younger food technologist may have no voice whatsoever. But the determination of the characteristics of a food that requires protection is definitely the responsibility of the food technologist. Corporation executives' views about packaging characteristics are frequently a trifle dilute.

Despite this responsibility for the preservation of food quality, the available tabular information of the needs for a food package, stated in terms of that food's packaging characteristics, is extremely limited. Doubtless this is due to the fact that the majority of present day food technologists have been concerned only with the rigid container (of long life) which has always been indispensable to heat sterilization. Thus the tin can and glass jar automatically obviate the need for study of many packaging characteristics. For we could not have had heat-preserved perishable foods without the rigid package.

As soon as we enter the field of foods suitable for being packaged in flexible containers we run smack into a host of problems of a much different nature, which today are solved almost entirely by trial and error. If food technologists—or shall we say food technology—were abreast of the needs of the day there would be systematic research on packaging characteristics, and a vast amount of data would be available to permit short cuts to packaging success rather than the time-honored and costly system of trial and error.

Materials handling cannot be logically separated from packaging, even though it is definitely within the field of mechanical engineering, for the reason that packages of food must be moved and handled after filling and closing. The selection of any package without due consideration of the correleated materials handling problems is often likely to be a more expensive choice than one based on an integrated knowledge of the two.

It is gratifying that a few of the institutions now teaching food technology are beginning to consider packaging in its proper place in food technology. All must ultimately do it. And those individuals who have already embarked in industrial careers must train themselves sufficiently so that their judgments will not overlook the final disposition of their products.

Admittedly, packaging and materials handling are only a part of the chain of indispensable attributes of a well-rounded food technologist, but they have not yet received the recognition or study that they should.

L. V. BURTON, *President I. F. T., 1941-42.*

Use of Ion Exchangers in By-Product Recovery from Pineapple Waste[a]

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Tests on using ion exchangers for recovering canning syrup and citric acid from pineapple cannery residue juice are described. Chemical data and an outline of the process are included.

Introduction

The introduction of stable high capacity ion exchange resins opened up new possibilities in the recovery of valuable by-products from cannery waste materials. The exchangers may be used to separate and concentrate constituents which are present in such low concentrations that they cannot be economically recovered by other methods. They may also be used to remove small quantities of impurities from the solution of a valuable non-electrolyte such as sugar. Both types of application are found in the operations on pineapple waste. In this instance the major component, sugar, is obtained in a relatively pure solution and is concentrated to a syrup which is used on the canned pineapple. In the same operation, citric acid is recovered from one of the regenerant solutions.

The pineapple waste consists primarily of the shell of the fruit and other inedible parts. Material which enters the by-product plant amounts to about 40% of the weight of the pineapple as received at the cannery. This waste is passed through screw presses which extract about 50 gallons of juice per ton of fruit processed. The pulp from the presses is dried and used for cattle feed. The by-product juice is screened to remove a part of the fibrous material which it contains. It is then heated to about 190° F. to precipitate heat coagulable material and after the addition of filter aide is filtered to yield a clear acid juice.

The by-product juice has a solids content of about 11%. These solids consist of about 75-85% sugars, 7-9% citric acid and smaller amounts of malic and hydrochloric acids, potassium, calcium, magnesium and proteinaceous compounds. This juice has a color which is slightly darker than that of beverage juice. The sugars are about half sucrose and half reducing sugars. This combination makes the recovery of any sugar by crystallization very difficult.

This acid juice has been used in the past as a medium for dissolving cane sugar to make up the cannery syrups. Since this use could provide an outlet for less than one-third of the supply, in some canneries the juice was decolorized with carbon and concentrated to yield higher density syrups that could be entirely used up on the pineapple pack. In other canneries the excess juice was either concentrated and sold for livestock feed or was discarded to the sewer. The carbon treatment fails to remove many of the impurities which are prejudicial to the production of a syrup of the highest quality. Some of these impurities are especially harmful in that they accelerate the development of off flavors during storage of the canned pineapple products.

The use of suitable ion exchange resins to remove the impurities from the by-product juice produces an excellent quality sugar solution which can be concentrated to a syrup that is far superior to those obtained by carbon treatment. One of the arguments which has been used by supporters of the carbon treatment in comparison with the ion exchange process is the fact that the carbon removes only a small fraction of the 15-25% of non-sugar solids in the juice. Since these solids are concentrated and added to the canned pineapple, they contribute to the density of the finished product. They therefore are utilized to replace an equal weight of sugar. The ion exchange treatment is more expensive than purification with carbon; however, the superior quality of the syrups obtained appears to be ample justification for the use of the process by the pineapple industry.

The early research work disclosed that certain problems are encountered in the use of ion exchange resins with by-product pineapple juice which had not previously been reported in treating other sugar-bearing solutions such as those of the beet and cane industries. The most striking of these problems was the fact that all of the cation exchangers tested suffered severe losses in capacity. These losses might amount to as much as 25% in the first cycle and would continue to build up during subsequent runs, although at a slower rate. This decrease in capacity was accompanied by a falling off in quality of the treated solutions. This difficulty was traced to the adsorption of compounds which were not removed by the usual acid regeneration. These compounds are dark colored and possess undesirable flavors. It was found that these troublesome impurities could be largely desorbed by treatment with alkaline solutions.

Another problem in developing the application of ion exchangers to pineapple waste was due to the losses in capacity shown by many of the anion exchangers. These losses were at a much slower rate than those described for the cation exchangers. However, in some cases they amounted to 25% in 100 cycles. This loss is probably partially due to the action of the reducing sugars present in the waste juice. The most stable anion exchanger found was one which had been developed to withstand the degradative action of reducing sugars. This exchanger is Duolite A-3 which is produced by the Chemical Process Company.

The ion exchange purification of filtered juice from pineapple waste can be carried out in two different ways. The acid juice may be treated directly and the citric acid recovered entirely from the anion regenerant solution or a part of the citric acid can be precipitated by lime before passing through the exchanger beds. The solubility of calcium citrate prevents the recovery of more than 60-70% of the citrate by lime precipitation.

[a] Presented before the Eighth Annual Food Conference, Philadelphia, Pa., June 7, 1948.

The lime which remains in solution after the precipitation and filtration increases the cation content by about 50%. This decrease in anion and increase in cation loads is advantageous from the standpoint of the initial plant investment since the cation exchangers are much cheaper than anion exchangers. It is also desirable from the standpoint of chemical requirements for the recovery of calcium citrate. The liberation of the citric acid from the exchangers requires about one equivalent of alkali and a calcium salt such as calcium chloride must be added to precipitate the citrate. The combined costs of alkali and calcium chloride are appreciably greater than the costs of lime for direct precipitation plus the additional sulfuric acid which must be used for the cation regeneration in operating on limed juice. Therefore, the process adopted included the lime precipitation of citrate before the ion exchange treatment.

Ion Exchange Process

The ion exchange process as carried out on the juice from pineapple waste consists of the following steps:

(1) Demineralization with two pairs of exchanger cells. This phase includes the sweetening on and sweetening off of the beds.

(2) Regeneration of the cation and anion beds in series with a sodium chloride solution from which calcium citrate is subsequently precipitated.

(3) Backwashing and draining of the resin beds.

(4) Alkaline rinse of the cation exchanger to remove adsorbed organic compounds.

(5) Sulfuric acid regeneration of the cation resin.

(6) Sodium hydroxide regeneration of the anion resin.

Since the calcium citrate precipitation and filtration are carried out hot due to the lower solubility of the citrate at high temperatures, the clear filtered juice is cooled in two spiral heat exchangers before entering the ion exchange cells. In the first heat exchanger it is cooled by the treated juice as it is being pumped to the evaporator supply tanks. The second heat exchanger is cooled by brackish water obtained from shallow wells.

The cooled juice is stored in a holding tank from which it is pumped through the exchanger cells. This tank receives not only all of the raw juice as it enters the plant but also the returns from all of the sample lines and the high Brix juice which is obtained on sweetening off an exhausted pair of cells.

The cooled juice is passed through two pairs of exchanger cells in the sequence, cation, anion, cation, and anion. The flow rate is varied depending upon the speed of the cannery operations. The flow rate is set on an automatic controller. The ion exchange cells are 10 feet in diameter and 10 feet high. They have a saran pipe under-drain system which is covered by slightly more than one foot of anthrafilt on which the exchanger beds rest.

The sweetening on operation is controlled by a density meter and the water from the cells passes into the sewer until its sugar concentration reaches 2° Brix. The purified solution above this concentration is diverted into the treated juice tank and is subsequently sent to the evaporator.

The first cation exchanger serves to remove the bulk of the inorganic bases. The effluent from this cell has a pH of about 2.0 at the start of a cycle. The potassium content of the juice is reduced by the first cation from over 1500 ppm. to less than 5 ppm. There is a slightly higher leakage of sodium. The break-through of the inorganic cations is quite sharp with sodium appearing in increasing quantities slightly before the potassium and calcium.

The removal of colored impurities by the first cation is much less complete than is the removal of inorganic bases. It is the removal of these compounds by the second cation exchanger that makes a double pass system desirable for the production of a good quality sugar syrup.

The first anion exchanger removes the liberated acids and also a considerable portion of the colored impurities. The anion exchangers remove a much larger portion of the colored compounds than the cation exchangers. However, if the cation exchangers have become fouled so that they are not efficiently removing color the anion beds cannot satisfactorily remove these impurities and a poor quality juice results. The pH of the anion effluent will vary from about 10 at the start of a run to about 5.0 at the end. This pH will vary with the amount of rinse water which has been used in the previous regeneration and is also affected by the type of organic acids which are present in the juice. With weakly held acids the pH may drop quite rapidly.

The second cation effluent has a pH between 3.0 and 3.5 and an acidity less than 0.01 N. The sodium and potassium are present only in traces.

The second anion effluent is almost free of colored impurities. Its low ash content is indicated by the specific resistance which is between 5,000 and 20,000 ohms. The pH of the second anion effluent is adjusted automatically by mixing in a small amount of second cation effluent. This step is taken in order to avoid heating an alkaline juice which would lead to a decomposition of some of the reducing sugars. The Brix of the treated juice averages about 8.0.

The juice cycle is controlled by the pH of the first cation effluent. The run is stopped when the pH rises to 3.4. The juice remaining on the pair is sweetened off into a sweet water tank from which it is slowly blended back into the raw juice tank. The sweetening off step is controlled by conductivity. This control is possible because the electrolyte content of the juice varies with the density. A conductivity control is not possible in the sweetening on operation since the electrolytes have been almost completely removed.

In the sweetening off all of the solutions below 3° Brix are discarded. However, the use of at least a part of these sweet waters is contemplated in the future. With the present operating conditions the losses in dilute waters approach 2% of the solids entering the plant. This loss is not entirely made up of sugar.

The treated juice is concentrated from 8° Brix to 25° to 50° Brix depending upon the cannery syrup requirements. These final syrups have a light yellow color. A quadruple effect tubular high speed evaporator

capable of distilling over 250 gallons of water per minute is used for this operation.

The first step in the regeneration of the sweetened off exhausted exchangers consists of passing a sodium chloride solution through both the cation and anion cells. This solution serves to remove calcium from the cation exchanger and citrate and malate from the anion. The citric acid can be recovered in a volume of regenerant that is only about one-eighth the volume of the juice that has been treated in the cycle. Therefore, it is possible to obtain a concentration of calcium citrate which allows for precipitation of this compound on heating the brine. After filtering out the calcium citrate the brine is cooled and used in subsequent regenerations. There is a discard of part of the brine in order to prevent the building up of undesirable impurities.

After the conclusion of the brine step the cells are backwashed in the usual manner. The anion rinse water from the previous cycle is used for backwashing the cation cell. This re-use tends not only to conserve water but also makes use of the alkali which it contains.

The cation regeneration is continued with an alkaline treatment followed by a warm water rinse. A portion of the evaporator condensate is used for the warm water supply. This alkali rinse does not completely remove the adsorbed organic material but does permit the exchanger to retain a reasonable working capacity for these tenaciously held compounds. There is a wide variation in the capacity of the various cation exchangers for these organic impurities. The dense high capacity exchangers are much less effective than the less dense resins. In selecting a cation exchanger it is necessary in an application such as on pineapple waste to sacrifice a certain amount of capacity for the exchange of inorganic bases in order to remove these larger undesirable organic compounds and thus obtain a satisfactory treated product.

Five percent or stronger sulfuric acid is used for the regeneration of the cation exchanger. The acid is divided into three portions which are designated "twice used," "once used," and "fresh acid." The twice used acid is discarded after passing through the cation exchanger. The once used acid is returned to the twice used acid tank. The fresh acid is returned to the once used acid tank and the fresh acid tank is filled with the first portion of the rinse water. The fresh acid is brought up to strength by the addition of 60° Bé sulfuric acid.

The anion resins are regenerated with a 2% sodium hydroxide solution which is made by diluting a stock 25% caustic solution with water. The caustic solution is discarded to the sewer until the dilute rinse waters are saved for the cation backwash in the next cycle.

The anion and cation exchanger cells are rinsed at first separately and finally in series until the regenerating solutions have been satisfactorily removed.

The Hawaiian Pineapple Company's ion exchange plant was designed by the Dorr Company. It can be operated either manually or automatically. By manual operation is meant the opening and closing of valves and the starting and stopping of motors by the operation of switches on the control panel. The valves are Saunders type with a rubber diaphragm and are operated by air pistons which are controlled by solenoid pilot valves that are in turn actuated by switches or relays on the control panel.

The control panel also contains the flow controllers, flow rate indicators, conductivity meters, pH meters, a temperature recorder, density meter, and dials indicating the levels in all of the regenerant tanks. An annunciator board which indicates the stage of the process for each cell is in the center of the control panel.

The auxiliary equipment includes air compressors, tanks for dissolving solid caustic, a brine dissolving tank, and a sulfuric acid storage tank.

The plant was first put into operation in August 1947. This was near the end of the peak canning season. It has been operated whenever the cannery has run during the past off season. Over 1,100 tons of sugar have already been saved by the operation of the plant.

There are certain operating problems which are more difficult to cope with during intermittent operations than they are during steady running. Probably the most important of these problems is plant sanitation. All of the equipment which comes into contact with the juice must be well cleaned if the growth of microorganisms is to be avoided. The used resins also offer a favorable spot for the growth of bacteria, yeast or molds.

In conclusion it can be stated that although numerous operating problems have been encountered, no serious difficulties have developed. The plant has operated without any prolonged stops due to breakdowns. The quality of sugar syrup produced has been consistently good. However, a complete evaluation of the process cannot be made until after the conclusion of more extensive operations.

Ion Exchangers in Food Processes[a]

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Several processes in which ion exchange materials are applicable to the food industry are briefly discussed. A few limitations of the method are listed.

The food industry has found ion exchange processes very helpful in the past both for water conditioning and for numerous applications outside water treatment. These processes may be summarized as follows:

1. Removal of undesirable electrolytes from solution
2. Addition of specific ions to solution
3. Separation of electrolytes in solution
4. Recovery of valuable electrolytes from solution
5. Catalysis

It is the purpose of this discussion to illustrate how these ion exchange processes have been used by others in the food industry and to investigate some of the limitations involved.

History

The phenomenon of ion exchange was discovered in about 1850 by H. S. Thompson and J. T. Way *(23)*, agricultural chemists in England, during some work on soils. For about 50 years thereafter, no industrial use was suggested for ion exchange. In 1896, Harm *(7)* disclosed the use of a calcium zeolite for removing the alkali metal cations, sodium and potassium, from sugar beet juice in order to reduce the amount of molasses formed during sugar manufacture. Rumpler *(18)*, Gans *(5)* and Bachler *(1)* also used calcium zeolites for improving sugar yield during the succeeding 30 years. The introduction of another ion exchange process, the demineralizing process, in 1936, resulted in continued investigations of ion exchange in this problem of long standing.

Materials

Ion exchange may be defined as the "reversible interchange of ions between a liquid phase and a solid phase which does not involve any radical change in the solid structure." Ion exchange materials, as commercially produced, are generally granular solids having a grain size between 10 and 60 mesh. (U. S. Bureau of Standards). There are two different types of ion exchange materials, cation exchangers and anion exchangers. These in turn may be broken down into several broad classifications:

A. Cation Exchange Materials
   1. Inorganic cation exchangers
      a. Processed naturally occurring minerals such as the glauconites or greensands
      b. Synthetic inorganics such as the precipitated sodium aluminosilicates
   2. Organic cation exchangers
      a. Processed naturally occurring materials, such as the sulphonated coals
      b. Synthetic resin cation exchangers
         (1) Modified phenol formaldehyde resins
         (2) Sulphonated hydrocarbons
         (3) Carboxylic acid resins

B. Anion Exchange Materials
   1. Aromatic amine resins
   2. Aliphatic amine resins

The ion exchange materials classified above each have specific properties. Every application for ion exchange requires certain characteristics of the materials to be used and therefore the choice of the proper type of ion exchange material is extremely important.

Types of Reactions

There are four different types of ion exchange reactions:

1. Base Exchange, using calcium as an example

$$Na_2Z + Ca^{++} \underset{\text{regeneration}}{\overset{\text{reaction}}{\rightleftharpoons}} CaZ + 2\,Na^{+}$$

where Na_2Z represents the cation exchanger in the sodium exchange cycle

2. Hydrogen Exchange

$$H_2Z + Ca^{++} \underset{\text{regeneration}}{\overset{\text{reaction}}{\rightleftharpoons}} CaZ + 2H^{+}$$

where H_2Z represents the cation exchanger in the hydrogen exchange cycle

3. Acid Removal, using hydrochloric acid as an example

a) $R_3N + HCl \xrightarrow{\text{reaction}} 2(R_3NH)Cl$

b) $2(R_3NH)Cl + Na_2CO_3 \xrightarrow{\text{regeneration}} 2R_3N + 2NaCl + H_2CO_3$ where R_3N represents the alkali regenerated anion exchanger

4. Anion Exchange

$$2(R_3NH)Cl + SO_4^{--} \underset{\text{regeneration}}{\overset{\text{reaction}}{\rightleftharpoons}} (R_3NH)_2SO_4 + 2Cl^{-}$$

The exchange of anions is sometimes used in special applications work, but seldom in water work. In this reaction the salt of an anion exchanger (Reaction 3a) is used.

For carrying out base exchange, either the organic or inorganic cation exchangers may be used. Generally the cation exchanger is in the sodium exchange cycle,

[a] Presented before the Eighth Annual I. F. T. Convention, Philadelphia, Pa., June 7, 1948.

i.e. regenerated with sodium chloride brine, although any sodium salt may be used. Likewise, the base exchange reaction may be carried out with any other base metal cation in the exchange position by using the proper salt for regenerating the cation exchanger. For carrying out hydrogen exchange, however, only the organic types of cation exchangers are used because the inorganic exchangers are not sufficiently stable to the low pH of acid regeneration.

In the selection of good ion exchange materials, too much attention is frequently given to the capacity of the material. While high capacity is an important characteristic, there are other factors which are even more important. Stability or the ability of the exchange material to continue giving its original capacity, lack of color throwing, rate of reaction, completeness of reaction, and economy of operation, are some of the other important characteristics.

Types of Processes

There are five types of processes in which the reactions of ion exchangers given above may be utilized *(19)*. These are:

a. Removal of undesirable ionic impurities from solution.
b. Addition of specific ions to solution.
c. Recovery of valuable substances from solutions.
d. Separation of electrolytes in solution.
e. Use of ion exchange materials as catalysts or solid contact agents.

Removal of Undesirable Ionic Impurities

Most of the work on ion exchange in the food industry has been conducted on this proces. The largest use of ion exchange in the food industry and indeed in any industry for the removal of ionic impurities in solution is in the field of water treatment. A diagram of a modern Zeolite water softener is shown in Figure 1. The use of ion exchange for treating waters for boiler water makeup, cooling waters, washing solutions and rinse waters, and general process uses have been widely discussed in the literature. However, it might be well

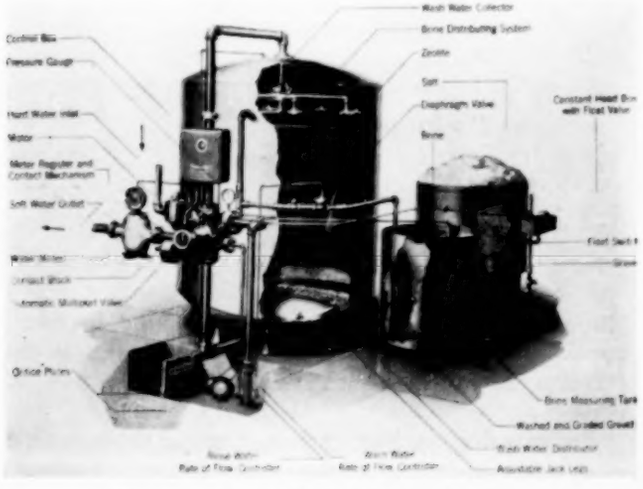


FIG. 1. Industrial Zeolite Water Softener.

to summarize here the importance of using water of the proper quality as ingredient in foods.

During recent years the distilling industry has found that demineralized water is just as good and in some respects better than distilled water, formerly used for deproofing alcohol. The cost of demineralized water is only a small fraction of that for distilled water. The soft drink industry has tightened its standards on the quality of conditioned water used in its products and in some cases ion exchange is used to produce suitable water.

In the canning industry, product quality improvement has also been realized by using properly conditioned water. For example, hard water in canning asparagus causes the buds to open whereas soft water keeps the buds tightly closed. The use of soft water in canning peas is extremely important because this vegetable has a considerable water softening capacity itself. The cellulose structure in the pea is said to take up the calcium and magnesium from the water in much the same manner as a conventional cation exchange material, the canned peas becoming tough and unpalatable. For this reason hardness is especially undesirable in blanching peas.

Base Exchange

The treatment of milk and milk products by base exchange has been used for altering the calcium and sodium content *(11)*. By exchanging sodium ion from an ion exchanger for calcium ions in milk, soft, easily digested curds are formed in the stomach rather than the hard tough curds often formed with cows' milk. This "softening" process has also been used to decrease the browning effects often noted in evaporated milk *(9)*.

Another promising use for base exchange in the alteration of the cation content of a solution is in the treatment of grape juice. By substituting some sodium for potassium and hydrogen in grape juice, it is possible to check the precipitation of potassium acid tartrate, which necessitates the extended storage of grape juice prior to bottling.

Base exchange has been found effective for the removal of heavy metals, for example lead from maple syrup *(24)*. The lead in maple syrup is introduced from the solder used in repairing evaporators and collecting pails. A calcium zeolite was found effective for removing 97% of the lead, reducing it below 1 p.p.m. (dry basis) without affecting the flavor of the maple syrup or changing the ash content.

Hydrogen Exchange

A unique process involving hydrogen exchange for the removal of undesirable impurities from solution has been in commercial use in the manufacture of pectin from grapefruit peel since 1941 *(14, 2)*. This is one of the few commercial applications where ion exchange materials are utilized in a batch-wise process not in a columnar operation. Figure 2 is a flow diagram of this process. The grapefruit peel is ground to particles approximately ¼" diameter which are then washed three times with hot water. The washed peel is mixed with water and Zeo-Karb, a sulfonated coal and extracted for an hour at 195° F. The hydrogen from the

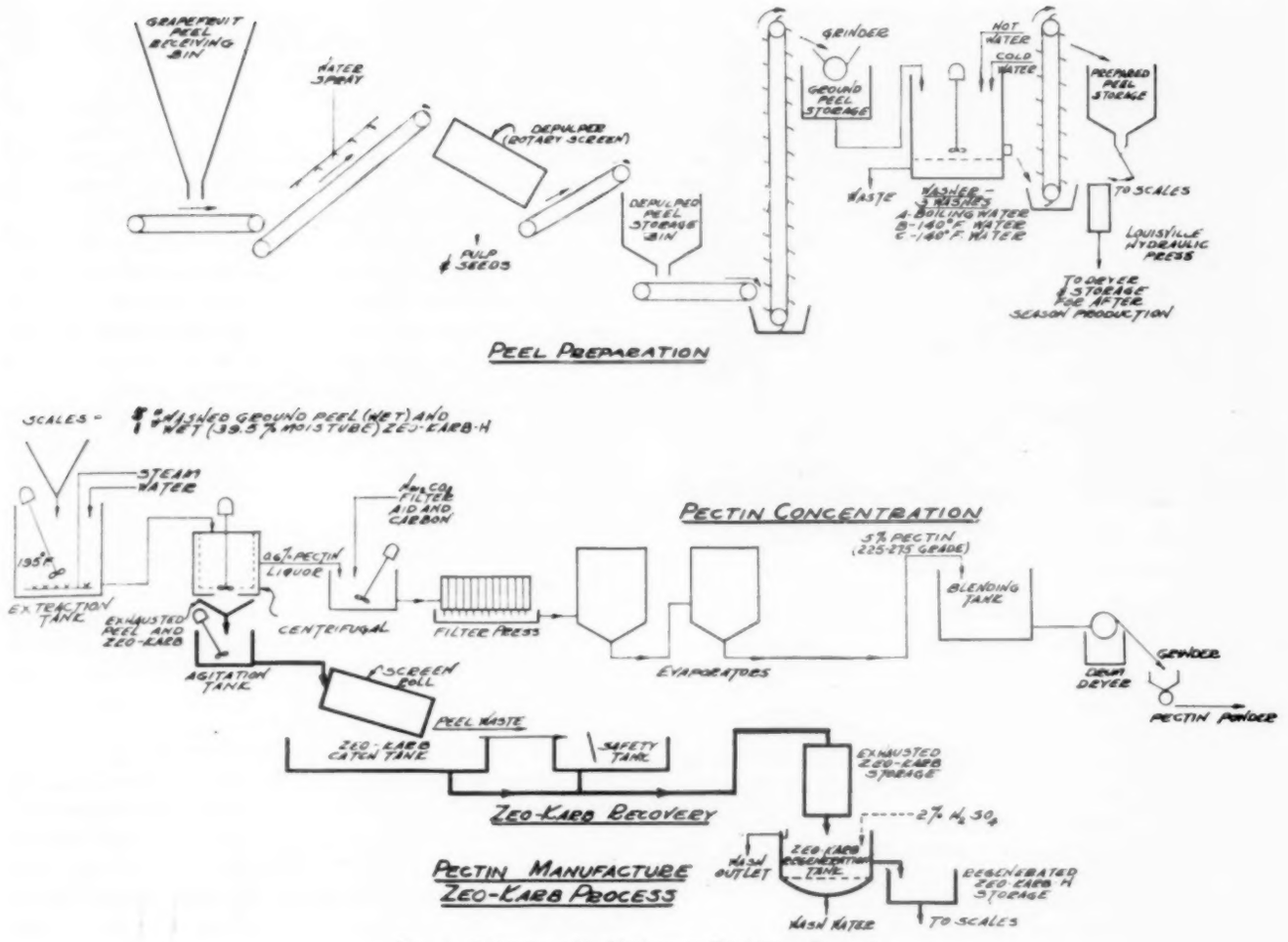


FIG. 2. Diagram of a Hydrogen Exchange Process.

Zeo-Karb exchanges for residual calcium and magnesium in the peel thus lowering the pH and causing the pectin to go into solution. The pectin solution is then separated from the exchanger and peel by centrifuging and the pectin is dried directly without going through the conventional precipitation step with alcohol or aluminum hydroxide. The use of this process results in obtaining a higher yield of a better grade of pectin. The spent peel and exhausted cation exchanger are separated to a certain extent on the porous wall of the centrifuge. The residual peel is separated from the exchanger in a screen roll and catch tank. The ion exchange material is then regenerated with sulphuric acid and rinsed for reuse.

Acid Removal

Acid removal by an anion exchanger is being used on a commercial scale for removing sulphuric acid from beta-alanine solution. B-alanine is used in the manufacture of pantothenic acid. The beta-alanine solution containing 1.2% sulphuric acid is partly neutralized with barium hydroxide. The resulting barium sulphate is separated from the beta-alanine solution by centrifuging and the residual sulphuric acid is removed by passing the solution through an anion exchanger unit. The product is sulphate-free as determined by barium chloride addition. An unexpected benefit of practicing this process is the complete elimination of evaporator foaming which previously was so serious that the constant attention of an operator was required at the evaporator station.

Demineralizing

The combination of the last two types of processes mentioned above, hydrogen exchange and acid removal, in a two-step process, constitutes the demineralizing process (sometimes called de-ionization). This process is being studied on a wide scale in the sugar industry, both beet and cane, for improving sugar yields; in the starch conversion sugar industry for improving yields, improving quality, and plant processes; in the fruit industry for recovering valuable products from waste materials; in polyhydric alcohol manufacture for improving product quality and widening the fields of use for the alcohol. The demineralizing process, as applied to the sugar industry, has been described in the literature in sufficient detail to eliminate the need for discussion here *(6, 13, 15, 17, 4)*. A typical water demineralizer installation is shown in Figure 3.

Addition of Ions

As a corollary to the removal of undesirable impurities by ion exchange, replacing these with more desirable ions, it is also possible to use these processes for the introduction of specific ions to solution. In wine

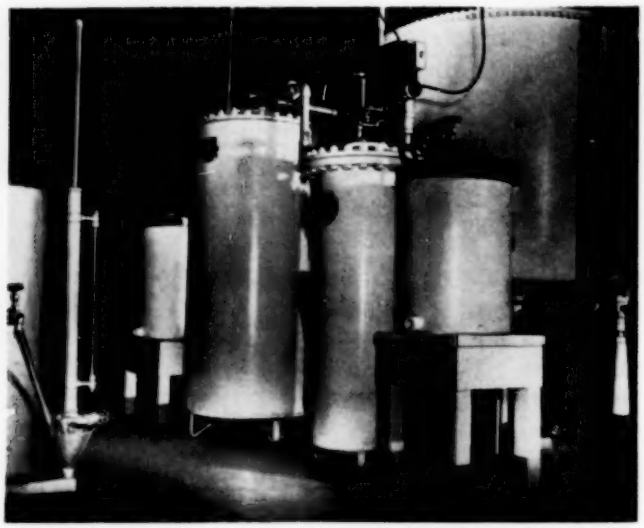


FIG. 3. Water Demineralizer.

manufacture, for example, the removal of iron may be accomplished by adding alkali to the wine to precipitate the iron and then treat the iron-free wine with a hydrogen exchange material to replace the hydrogen ions *(16)*. A process for purifying citric acid obtained from "decompose liquors," the product formed on adding sulphuric acid to calcium citrate, has also been disclosed. The "decompose liquors" are passed through a hydrogen exchanger where residual calcium ions are removed in exchange for hydrogen ions *(3)*.

Recovery of Valuable Substances

Ion exchange has been found extremely useful in recovering valuable substances from solutions. These recovery processes may be brought about by two means:

a. The adsorption of an ionic substance on the ion exchanger and subsequently the recovery of the material from the ion exchanger

b. The recovery may depend on the removal of impurities from the waste solution in order to purify and utilize a non-electrolyte, for example sugar, present in the waste solution.

Valuable acids, such as citric acid, malic acid, aconitic acid, lactic acid, and so on, may readily be recovered by anion exchangers either as the salts or as the acids directly. If the acids are present in the waste solution as salts, they must first be converted to the corresponding acid by passing the solution through a hydrogen exchanger and then through the anion exchanger for recovery. After exhausting the anion exchanger with the acid, it may be treated with

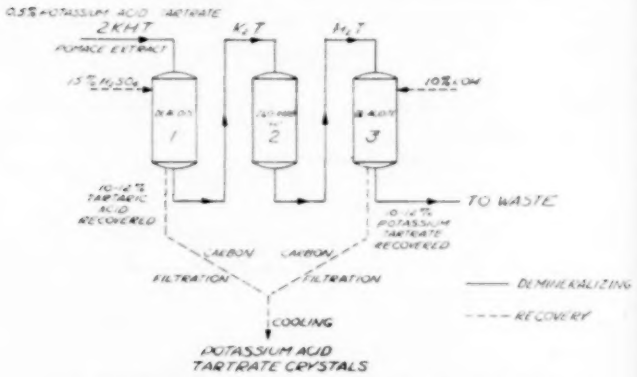
(a) a salt solution, such as sodium chloride, to obtain the salt of the organic acid and the anion exchanger salt

(b) an alkali, to obtain the salt of the organic acid and at the same time regenerate the anion exchanger to the base condition for reuse

(c) an acid, to obtain the organic acid directly, and the anion exchanger salt.

In processes (a) and (c) above, it will be necessary to regenerate the anion exchanger with an alkali before reuse in the recovery of valuable organic acids.

Tartrate value may readily be recovered by ion exchange, using either of two processes: (a) Passage of the tartrate wastes, potassium acid tartrate solution for example, through an anion exchanger salt bed such as the anion exchanger hydrochloride. The tartrate anion exchanges for the chloride anion, forming the anion exchanger tartrate. On exhaustion of the anion exchanger, a brine solution is passed through the bed and sodium tartrate is formed, at the same time regenerating the anion exchanger to the hydrochloride salt for reuse *(12)*. (b) An alternate process consists of passing the potassium acid tartrate solution through the three-step demineralizing process shown in Figure 4.



3-STEP DEMINERALIZING-TARTRATE RECOVERY

The first step consists of an anion exchanger bed, where the free acid in the potassium acid tartrate is removed, forming potassium tartrate solution in the effluent. This is passed through a hydrogen exchanger where the potassium tartrate is converted to tartaric acid which is then removed from solution by the third step, an anion exchanger. The first anion exchanger bed is treated with 15% sulphuric acid to form 8 to 10% tartaric acid solution. The other anion exchanger bed is regenerated with 10% potassium hydroxide to form approximately 10% potassium tartrate. These two solutions are decolorized hot, using activated carbon, mixed, and then cooled. On cooling, large crystals of pure potassium acid tartrates separate *(22)*. It is quite rare that a salt may be recovered in such a convenient manner since there are only a limited number of insoluble acid salts such as potassium acid tartrate.

Alkaloids and other nitrogen compounds such as some vitamins may also be recovered by ion exchange *(10, 8)*. For these processes, cation exchangers are generally used and very often it is necessary to employ liberation and solvent treatment of the cation exchanger in order to effect satisfactory recovery of the nitrogen compounds from the cation exchanger.

Separation of Materials in Solution

A great deal of work has been conducted on the use of ion exchange in the separation of amino acids. Tiselius and his co-workers *(21)* have devised a method

of separating a mixture of amino acids resulting from protein hydrolysis based on these considerations:

1. Only the aromatic amino acids are adsorbed on active charcoal.
2. From the filtrate, the basic amino acids (pI>7) are selectively adsorbed on a carboxylic acid resin.
3. The remaining amino acids (pI<7) are all adsorbed on a cation exchanger containing sulphonic acid groups.
4. Of the amino acids in group 3, only the polycarboxylic monoamino acids ((pI<5) are retained by anion exchangers.

Catalysis

The use of cation exchange in the hydrogen condition as "solid acids" for catalyzing certain types of reactions is a promising field. For several years, a sulphonated coal has been used in the esterification of butyl alcohol with a fatty acid. Several other reactions have been successfully catalyzed in our laboratories. Among these are alcoholysis, ester interchange, de-esterification, and acetal formation *(20)*. It is quite likely that such catalysis may be found useful by the food industry for the production of synthetic flavors and essences.

Limitations

The examples of ion exchange applications mentioned above cover only a few of those which are being studied and used commercially. There are hundreds of others which might be listed. Obviously, not all these applications are commercially feasible in all cases since other means for carrying out reactions are often cheaper. It may be advisable to list here a few of the limitations of ion exchange:

a. Ion exchange has not been succesfully employed as a continuous operation
b. Ion exchange shows up to best advantage in treating solutions having relatively low concentrations of impurities.
c. Dilution of solution being treated or recovered.
d. Amount of regenerant is of necessity greater than theoretical.

Summary

The examples discussed above illustrate how ion exchange has been used in the food industry. The most widespread use is in the removal of impurities but it is also possible to use ion exchange for the addition of specific ions to solutions, the recovery of materials from wastes, the separation of substances in solution, and in catalysis.

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Commercial Ion-Exchange Purification of Sugar-Bearing Solutions[a]

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A discussion of the various developments associated with the application of ion-exchange for purification of sugar-bearing solutions is presented. Typical analytical data pertinent to the discussion are presented.

The use of ion-exchange for the purification of sugar-bearing solutions has received major attention almost from the very moment of inception of ion-exchange principles, especially since the advent of acid-adsorbing resins. In the discussion to follow, I should like to outline in broad terms the growth and development of ion-exchange purification of sugar-bearing solutions with some specific technical data selected to illustrate the various points. Emphasis will be on developments with which Chemical Process Company has been most closely associated, especially those occurring in the Western area.

As early as 1940, Maui Pineapple Company in conjunction with Chemical Process Company began the investigation of the feasibility of salvaging sugar values from pineapple wastes, work which was not completed; but subsequently a similar project was carried on to successful conclusion by Hawaiian Pineapple Company.

Recovery of sugar values from fruit wastes by ion-exchange now seems slated to grow to respectable proportions, especially in the Western areas where water conservation drives are rapidly eliminating water pollution from food-processing and industrial wastes. For example, in the San Jose, California, area, the various packing plants have arranged to dispose of fruit wastes at a central plant. Such wastes assembled without regard for sanitation have but little commercial worth; however, sugar values recoverable by ion-exchange are present. There is a considerable margin over costs of chemical regenerants and plant amortization to pay for collecting and for other process charges. Perhaps the two most difficult technical problems to be solved consist of instituting proper sanitary measures in handling the wastes and of devising proper defecating techniques for the raw juice.

Mr. Henry Vallez, pioneer in the application of ion-exchange to the purification of sugar juices, climaxed years of bench and pilot plant studies with a semi-commercial test during the 1941 sugar beet campaign in the Mount Pleasant, Michigan, plant of Isabella Sugar Company in cooperation with Infilco, Inc. of Chicago. Also in the 1941 campaign Chemical Process Company operated a pilot plant in the purification of sugar beet juice in the Betteravia, California, plant of Union Sugar Company and about the same time The Dorr Company of New York was carrying on experimental work with The Amalgamated Sugar Company at the latter's factory in Burley, Idaho.

In the early part of 1942, Chemical Process Company, working jointly with Corn Products Refining Company, tested in a pilot plant setup the purification of corn starch hydrolysates in the latter's Argo factory—a study which demonstrated the need for an anion exchanger inert to irreversible reaction with dextrose.

Cooperative research involving The Dorr Company, Infilco, The Amalgamated Sugar Company and Chemical Process Company extended ion-exchange studies to include the treatment of raw and predefecated juice. As an outgrowth of this work, Amalgamated built their D. I. plant at Twin Falls, Idaho, in 1946 to handle diffusion juice directly by ion-exchange with the pectin and albuminous material precipitated by the pH drop in the cation bed being filtered out ahead of passage of the acid juice through the anion cell. As a result of delays in installing and the normal engineering difficulties incident upon starting a new plant, a complete evaluation of the process was not made—in fact, the only prolonged run which the plant was able to make extended from some time on Thursday, February 13, 1947, to about 4 p. m. Friday, February 21, a period when white sugar was made commercially without a pound of lime entering the house.

Excessive inversion losses were successfully prevented while retaining the juice in an acid state long enough to carry out the intermediate filtration between anion and cation. For example, a composite sample of raw diffusion juice from one 8-hour shift shows 1.78% invert while a composite sample of evaporator thin juice from the same period shows 1.98% invert, an increase of exactly 0.2%. A number of schemes for handling remelted raw sugars by recirculating through early steps in the process were also employed during the brief run, making it difficult to assess the purity gains. However, an apparent purity of 94.9% in the evaporator thin juice derived from deionization was noted during one period when the apparent purity of the diffusion juice ran in a range from 83.4 to 85.8%. It is not certain that this evaporator thin juice was free of impurities from remelted and recirculated low-purity sugars. The filtration of the acidified juice from the cation cell was carried out successfully, albeit at the expense of considerable filter aid, slightly under 1% on beets. There was no opportunity to determine whether this represented the minimum amounts usable. Precipitated albuminous material in the cells was quite easily removed during the backwashing, but the excessive foaming of the raw juice did create difficulties, which, however, would be easily solvable. Sufficient organic material escaped removal through ion-exchange and filtration to raise the turbidity of the final white sugar from a normal 2 p.p.m. to about 10 p.p.m.

During the period of extreme sugar shortage just past, the processing of beet and cane molasses into an

[a] Presented before the Eighth Annual I. F. T. Convention, Philadelphia, Pa., June 7, 1948.

unrationed confectioner's syrup by ion-exchange was extensively studied and the practice was adopted commercially in a number of places.

A pilot plant study which attracted considerable attention in the sugar industry was made in 1945 by American Cyanamid Company in cooperation with Holly Sugar Corporation in the latter's Alvarado, California, factory. A report of this study has been given by Riley and Sanborn *(7)*.

The use of exchangers to purify corn sugar liquors has gone forward, meanwhile, in both enzyme and acid hydrolyzed starches with hot processing gaining attention in this field. The Illinois Water Treatment Co. built a plant for purifying maltose at Waverly, Iowa, and Corn Products Refining Company has been making extensive and large-scale pilot plant investigations of ion-exchange production of dextrose in their Argo factory, studies which have led to commercial plants now under construction at Pekin, Illinois, and Corpus Christi, Texas. Increased shelf-life and a better quality of product are the attractive features of ion-exchange to the corn sugar industry.

Second carbonation juice was treated in the Hardin, Montana, plant of Holly Sugar Corporation and the Layton, Utah, plant of Layton Sugar Company, during the 1947-48 campaign, answering on a commercial scale questions regarding increased extraction, regenerant consumption, amount of inversion, dilution, etc. Representative results from these two operations are summarized in Table 1 *(3, 5)*.

TABLE 1

Average Performance of Commercial DI Plants in Purification of Second Carbonation Beet Juice

	Hardin Plant		Layton Plant	
	Influent	Effluent	Influent	Effluent
Brix	12.5	9.6	13.0	11.8
Sugar	11.0%	9.5%	12.1%	11.6%
Purity	89.6%	97.6%	93.8%	98.6%
Non-sugar removal	.....	82.5%	.....	77.6%
Nitrogen-removal	.....	56.0%	.....	.....
Ash-removal, approx.	.....	94.0%	.....	.....
Dilution	.....	13.6%	.....	.....
Invert	.....	.....	0.13%	0.36%

Intermediate syrup from the sugar house rather than second carbonation juice was selected for purification by ion-exchange in the West Jordan factory of the Utah-Idaho Sugar Co. *(1)*. The purified juice was returned to the thin juice going to the evaporator.

Their results are summarized as follows: By handling one-fourth of the machine syrup through a DI plant and returning the purified effluent to the incoming second carbonation juice, some 20% of the impurities entering the house were removed by deionization, and gave an increased sugar yield of 4.04% based on the average extraction for the previous 10-year period, or 4.7% based on the average extraction for the previous 5-year period. The results at Hardin and Layton show a non-sugar removal between 77 and 83%, and it is thought among the more optimistic people in the sugar industry that such a non-sugar removal can be made to lead to an increased extraction of perhaps 11% over a straight house.

Some of the problems encountered in the campaign were rather surprising. Although more white sugar was secured without remelting from the deionized effluent than is possible from standard juice, staining did occur on crystals boiled from intermediate syrups possessing higher purities than the juice which enters the white pan in conventional houses where highly colored juices of 89 to 94% purity give white crystals. Also, despite the 50-60% nitrogen-removal effected by deionization, color did develop rather quickly and intensely upon boiling, an effect apparently catalyzed by iron since it was greatly mitigated when the deionized juice was concentrated in glass. The small quantity of invert formed by deionization may enter into browning reactions with nitrogen-containing molecules to form color bodies of high staining propensity. Normally such invert as enters the house from low-quality beets is destroyed by heavy liming. The cane industry has always had to contend with high invert and colors with pronounced staining tendencies. The suggestion was also made during the campaign that the deionization was removing impurities which normally buffered against color staining of the crystals. A number of solutions to the color problem are indicated as being feasible. More rapid handling of the juice during sugar-boiling would minimize color-formation. It can be inhibited to a certain extent by post-deionization treatment. A more complete nitrogen-removal would further minimize the problem.

Perhaps the most promising of the proposed solutions to the color problem lies in the isolation of nitrogen-containing molecules in the initial stages of deionization. Nees and Bennett *(6)* have indicated a method for isolation and concentration of glutamic acid from Steffens house waste. The waste is run into a cation cell until the nitrogen breakthrough occurs. Then the effluent is collected in a separate nitrogen-rich fraction with the Steffens house waste continuing to enter the top of the cation cell so that its ash content can dislodge the nitrogen which has collected in the bottom zone. When the cell is completely loaded with Steffens house ash, with all the nitrogen pushed out into the nitrogen-rich fraction, then it is rinsed to remove untreated material for recycling, and regenerated. Meantime, the nitrogen-rich fraction is run through a fresh cation cell until nitrogen breakthrough occurs. It is then shut down and the carbohydrates are washed out. The glutamic acid is stripped from the second cell with ammonia in a relatively pure state, some seven or eight times as concentrated as in the original solution. The ash from the nitrogen-rich fraction is left in the second cell.

The Dorr Company in their Westport Laboratory have been studying the distribution of the nitrogen pickup from factory thick juice among the various exchanger beds and regenerant liquors with the results shown in Table 2 *(4)*. Nitrogen-removals of these magnitudes were made with thoroughly regenerated beds. The cation bed is removing well over half the nitrogen content including the valuable glutamic acid and small quantities of glutamine which are convertible to glutamic acid. The anion bed handles among other

TABLE 2

Distribution of Nitrogen Removed by Ion-Exchange from Thick Juice

	1st Factory	2nd Factory
Nitrogen in ammonia used to strip cation bed ahead of regeneration	0.170	0.104
Nitrogen in waste acid cation regenerant	0.004	0.004
Nitrogen in waste anion regenerant	0.089	0.062
Nitrogen in deionized juice	0.010	0.006
	0.273	0.176
Nitrogen in original thick juice treated	0.278	0.178

Units referred to equivalents nitrogen per liter of thick juice.

constitutents pyrrolidone carboxylic acid, also convertible to glutamic acid.

We now consider that it may be desirable to split the cation function in beet sugar refining into three parts: Lime salts which are very inefficiently removed with a sulfuric acid regenerant from ordinary strong-acid-type cation exchangers can be handled by a cation exchanger, such as our Duolite Cation Selector CS-100, which depends for its ion-exchange activity on weak acid groups. This material, which selectively removes the divalent ions over the monovalent ones, and almost quantitatively so long as the pH is buffered against dropping by suitable anions, is efficiently regenerated with dilute acid, perhaps by the waste acid from the standard DI unit. Some of the cation exchangers showing high ash-removal capacity are very poor on picking up molecules containing nitrogen and could thus be utilized in the second phase of the cation exchange for removing the metallic cations, allowing most of the nitrogen to escape by leakage. Finally, a cation exchanger especially adapted to handle large nitrogen-containing cations could complete the exchange and the nitrogen molecules could be stripped in a fairly pure and concentrated solution by the use of ammonia. Acid adsorption may need to be interposed in the process.

Other than some complications in engineering, the chief drawback to the proposal may be a tendency to increase invert. It has been observed that the hydrogen form of a high capacity cation exchanger is an excellent catalyst to promote the inversion of sugar but that impurities in the influent reduce greatly such inversion; hence the universal adoption of the single-pass method of purifying beet sugar juices. Regardless of merits of the above proposal, or modifications of it under consideration, it is desirable to effect as complete a separation of the nitrogen fraction in the initial stages of deionization as possible, both to reduce color problems and to isolate a valuable by-product, glutamic acid.

Sugar cane juice has been subjected to much investigational work in ion-exchange but handicaps in applying this method of purification arise from the high cost of regenerants prevailing in many cane-growing areas as well as the refrigerating costs in cooling juices to prevent inversion. Further, in Cuba the amount of raw sugar which the island is permitted to export to the United States fixes production rather than any limitation of acreage or extraction per ton. Ion-exchange does offer some promise in refining raw cane sugar, however, especially in permitting installations for sugar-refining much smaller than present bone char plants.

Considerable attention has been given to maintaining the capacity of exchanger beds in the treatment of the complex sugar-bearing solutions. It has long been recognized that organic bases are taken up so strongly by the cation exchangers from certain types of solutions that the ordinary acid regeneration is insufficient to dislodge them and it is necessary to resort to occasional caustic rinses to prevent poisoning of the cation bed. It has also been recognized that certain undetermined compounds can be adsorbed and held so tenaciously by the anion bed that they are removed with difficulty by caustic regeneration and therefore frequent acid rinses with mineral acids have been recommended.

In connection with anion poisoning, a recent conversation with Dr. M. Calvin of the University of California concerning some photosynthesis work which he is carrying on with the green algae *Chlorella (2)* revealed information that seemed significant. Dr. Calvin was employing ion-exchangers in the fractionating and isolation of various products formed by the algae. He found that on the Duolite A-3 which he was employing, considerable quantities of triosephosphate, hexosephosphate and phosphoglyceric acid were adsorbed. The first two acids are readily elutriated with ammonia while the phosphoglyceric acid can be removed only with sodium hydroxide. Dr. Calvin tested a number of acids which probably occur in sugar-bearing solutions and found that the phosphoglyceric acid is the only one not removable by ammonia although large excesses of this latter regenerant may be required. Dr. Calvin's observations are suggestive in view of the fact that the anion beds in some of the sugar installations tend to become poisoned when used with ammonia regenerant alone.

It seems to be essential in extending the life of ion-exchangers to maintain the beds in a clean condition. Cation exchangers which have become fouled with nitrogen-containing molecules and have been allowed to remain in such a condition have shown a distinct tendency to lose sulphur while, conversely, poisoned anion beds seem to lose active nitrogen. Is this a bacterial action or is it due to the formation of very stable amides which weaken the primary bonds of attachment?

At Layton a hot water backwash was employed to keep the beds free of waxes and other materials which might clog the exchanger mechanically.

The role of ion-exchange in color, odor and taste refining of sugar-bearing solutions has been an unforeseen but important development.

Mr. E. R. Stadtman has described some experiments which Miss Victoria A. Haas and he have carried out in the Department of Food Technology at the University of California, in which they employed ion-exchange to study the nature of browning reactions. Using an apricot concentrate, they were able to split the color precursors into a cation fraction containing some 81% of the nitrogen, an anion fraction containing 88% of the acids other than the amino acids, and a neutral fraction containing 98% of the sugars. By blending these various components and studying the rate of color-formation, they were able to make some very fundamental deductions regarding the nature of browning reactions. They have demonstrated that the overall browning is

a summation of at least four distinctly different types of reactions involving reactions between nitrogen-containing molecules and sugars, between nitrogen-containing molecules and organic acids, between sugars and organic acids, and reactions involving only organic acids. As often suggested, glucose is an important constituent of the neutral fraction contributing to browning, but the organic acids have roles of varying importance in contributing to the overall effect. When stored separately, the fractions showed but slight tendency towards color-formation.

The general observation can be made that the nitrogen-containing molecules do tend to be removed from sugar-bearing solutions on the cation bed as the work of The Dorr Company and of Haas and Stadtman already quoted above emphasizes, while many of the color bodies tend to be removed on the anion bed; this is especially true with beet sugar.

As an example of the relationship between color-removal and the adsorption of mineral acids, the data from our own laboratory are given in Figure 1. It will be observed that the anion beds are handling the removal of the particular color bodies under study in a striking manner in addition to their more conventional mineral acid adsorption.

A recapitulation shows that the four sources of sugar-bearing solutions—beet, fruit wastes, starch hydrolysates and cane—have been extensively investigated by bench and pilot plant work and commercial development is actively under way in the first three. Bed maintenance problems are being adequately met. An important supplementary function of the ion-exchangers is to remove nitrogen-containing compounds on the cation bed and color bodies on the anion bed, and to carry on taste and odor refining.

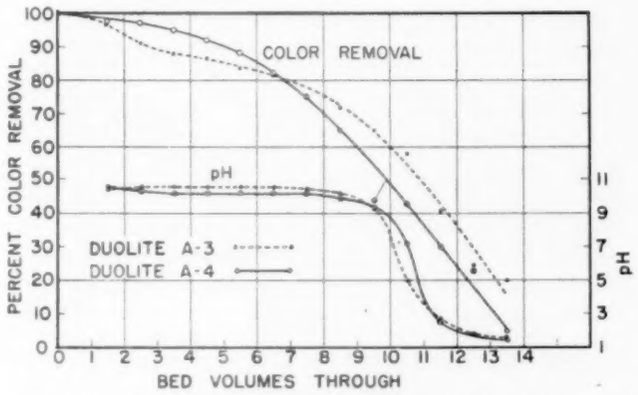

FIG. 1. Simultaneous de-acidifying and decolorizing of "Hydrol" diluted 1:20 and acidified to 0.115 N with HCl. Flow rate = 4 bed volumes per hr.

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Pressure Hydrolysis of Proteins[a]

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The possibilities of improving the hydrolysis of proteins with higher pressures and temperatures, such as 75-80 p.s.i. and 180°C., are indicated. A continuous system, whereby hydrolysis might be effected without previous alteration or destruction of the protein molecule, is suggested.

There is considerable literature on the high pressure hydrolysis of various organic substances, but the information is meager concerning the effect of high pressure on proteins. Studies by Sherrard and Blanco *(12, 13)* on the hydrolysis of wood cellulose with water, and, dilute and concentrated acids, have shown that they obtained very nearly the same amount of reducing sugar with 5% HCl at 115 pounds steam pressure in twenty minutes as that obtained by refluxing with 5% HCl in six hours at ordinary pressure. They conducted many studies on the hydrolysis of wood at high pressures and temperatures, and reported vastly accelerated hydrolysis and unobvious reactions.

The cracking of petroleum with high pressure and temperature has produced tremendous volumes of olefine gases most of which have been used for fuel, but which are becoming increasingly valuable as raw materials, particularly for alcohol production. The subsequent effect of these cracking processes on the growth of the petroleum industry is well known and has been given wide publicity.

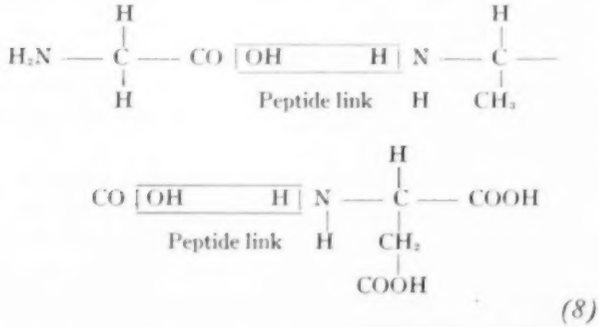
The hydrolysis of carbohydrates such as starch and sugar with high pressure and temperature is described by Walton *(14)* and practiced to an advantage as in the Scholler-Tornesch Process *(5)*. Corn starch itself may be subjected to hydrolytic processes which convert the starch to dextrins, corn syrup, and corn sugar. The hydrolysis is accomplished by acidifying the starch with dilute hydrochloric acid and subjecting the material to steam under pressure.

[a] Presented before the Eighth Annual Food Conference, Philadelphia, Pa., June 9, 1948.

Ipatieff *(7)* and others have shown that many chemicals are manufactured through catalytic reactions using high pressure and temperature, and that the synthetic hydrogenation of some organic substances are facilitated.

The hydrolysis of proteins has been practiced for many years, primarily by three methods (1) boiling with acids, (2) boiling with alkalies, and, (3) the action of proteolytic enzymes. Commercial protein hydrolysates as shown by Hall *(6)* have been manufactured in this country since about 1935, and much earlier in Japan and China. In more recent years, low pressure equipment for protein hydrolysis has been available and hydrolytic reactions have been conducted at 10 to 25 pounds pressure at temperatures ranging from an average of 108° C. to 125° C. Reaction time has therefore been decreased from about 14 to 16 hours to from 5 to 6 hours when the hydrolyzing acid is 20 to 25 percent HCl. This has been important from a profitable production standpoint, but little has been learned regarding the flavor value of the resulting hydrolysate, the liberation of certain amino acids, and, the alteration or destruction of the amino acids.

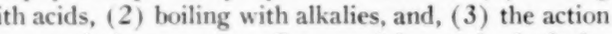
Protein molecules consist of hundreds or even thousands of amino acids. While an examination of the nature of the hydrolysis products has contributed much to our present knowledge regarding the structure and chemical composition of the protein molecule, there remains much work to be done. Investigations from the work of Kossel, Fischer, Abderhalden, Osborne, Svedberg, Bergmann and others have given results leading to the conclusion that the proteins consist of amino acids linked together by means of the carboxylic group of one and the amino group of the other with a simultaneous loss of water, and, further, that secondary valence forces have an important role in the formation of characteristic patterns which are associated with the various proteins. The early postulate of Emil Fischer *(2)* that proteins consist of long chains of amino acids bound through a peptide or amide linkage is still generally accepted. This theory is acceptable on the observation that proteins contain very few free amino and carboxyl groups in contrast with the large number of groups of both types present in the hydrolysate mixture and since, on hydrolysis, amino and carboxyl groups are liberated in equivalent amounts. The manner in which the amino acids are linked to form peptide chains may be indicated in accordance with Example I.



(8)

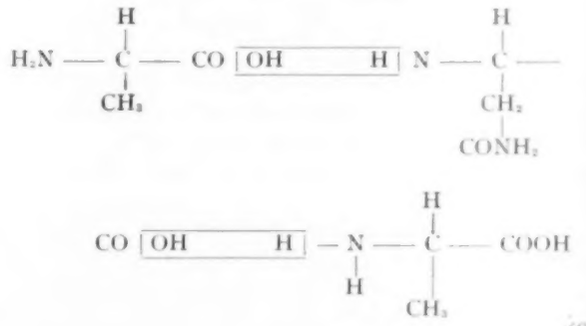
On hydrolytic cleavage, the peptide linkages present in the protein molecule are broken and the constituent amino acids are liberated. In this process, the original protein unit is broken down to proteoses, peptones, and peptides, into the amino acids.

In Example II it is to be noted that ammonia, another compound found in protein hydrolysates, is formed mainly by the hydrolysis of the acid amide group:



The quantity of ammonia parallels the amount of dicarboxylic acids.

In accordance with Example III the carboxyl group of dicarboxylic amino acids not involved in the formation of peptide linkages is found principally in the acid amide form. Although a small amount of ammonia may be produced by the action of acids on the monoamino acids, by far the largest amount is due to the hydrolysis of the acid amide group. The existence of acid amide groups in chains may be indicated as follows:



(9)

It has been demonstrated by Gordon and coworkers, and by Lugg *(3, 10)* that there is an alteration of the amino acid residues during hydrolysis and in certain instances there is destruction of some of the amino acids. The effects of this alteration and decomposition or destruction still remain a problem for further research study in the proper evaluation of hydrolytic reactions.

In studies on the production of hydrolysates, our interest in the effect of high presure and high temperature was primarily from the standpoint of substantially accelerating the hydrolysis time and thus improving the production economics. Predicating our work upon substantial information and data from many sources where such reactions had been successful experimentally and industrially, we realized the potentialities of hydrolysate production of an improved character, and also the possibility of less troublesome extraction of glutamic acid and other amino acids.

It is not our purpose here to discuss in detail the theoretical chemistry of the hydrolysis of proteins by high pressures. We are concerned mainly with presenting the data of some two dozen or more hydrolytic experiments carried out under varying conditions which are by no means complete.

It is well known the higher the temperature, the faster is the rate of hydrolysis. The most frequently used procedure of hydrolysis has been to boil and reflux the mixture containing the catalytic agent and the protein until the reaction is completed. It is known that the rate of hydrolysis can be increased if the mixture is heated under presure. Since time is a factor, it is preferable not to continue hydrolysis beyond the time

required for its completion. The hydrolysis of proteins with acids, and, under certain conditions, with alkalies, under steam pressure has definite advantages over hydrolysis by boiling and refluxing.

Studying the effect of temperature on the rate of acid hydrolysis of gelatin, Greenberg and Burk *(4)* demonstrated that the velocity constant is a function of temperature and can be expressed by the following equation:

$$\text{Log } K_a = 0.0287\,T - 5.30$$

in which K_a refers to the velocity constant at unit activity and T is expressed in degrees centigrade. Obviously there is considerable economy in time and material when proteins are hydrolyzed by acids or alkalies under steam pressure and at an elevated temperature, not sufficiently high to alter the protein prior to hydrolysis.

Dunn *(1)* has investigated the rate of hydrolysis of casein by acids and on the basis of his measurements reported that it was a first-order reaction. Greenberg and Burk *(4)* studied the hydrolysis of gelatin, gliadin, and silk fibroin by different concentrations of hydrochloric acid and sulphuric acid. Their data indicated that the rate of hydrolysis of these proteins measured by the increase of amino nitrogen was that of a second-order reaction. They also showed that the catalytic action of acids in protein hydrolysis is proportional to the activity of the hydrogen ion. Nassett and Greenberg *(11)* reinvestigated the acid hydrolysis of casein and found that its rate conformed to the equation for a second-order reaction:

$$K = \frac{1}{t} \times \frac{x}{100 - x} \times \frac{1}{100}$$

in which x represents the percentage of protein hydrolyzed in time t.

It is well known that the hydrolysis of a protein is considered complete when the peptide linkages are entirely broken. This is rather difficult to determine accurately. The Biuret test is useful and frequently employed for this purpose, but it is not conclusive. One of the best methods for determining the completion of protein hydrolysis is the estimation of the amino nitrogen by means of the Manometric Van Slyke apparatus, and this has been used in our work.

Experimental

Figure 1 shows the high pressure equipment (A Pressure Bomb and Shaker) used in our experiments. The equipment is widely used for synthetic hydrogenation of organic substances and for facilitating the investigation of high pressure catalytic reactions. It is so constructed that the bomb in which the reaction is taking place can be heated, and at the same time the mixture within can be agitated. The bomb is rocked through an angle of approximately 30° at a rate of 58 times per minute which is obtained by the use of a one-quarter horsepower induction motor with built-in reduction gears. There is a pressure gauge mounted between the inlet valves and the pump so that reaction pressure may be determined at all times. The flask or liner used inside the bomb is made of heavy pyrex glass especially built to withstand high pressures and temperatures.

FIG. 1. Superpressure equipment for pressure hydrolysis of organic substances. For pressures up to 22,000 lb. per sq. in. For temperatures up to 500° Centigrade.

Wheat gluten, the only protein used in our studies, contained approximately 85% protein and was a light colored material of about 40 mesh fineness. In all tests, ¼ lb. of gluten was mixed into a paste with 350 ml. of liquid.

Table 1 gives the results of tests with water as the hydrolyzing medium. After the gluten was mixed into a paste it was placed into the pyrex glass tube and heated in the bomb to the desired temperature which was maintained for 30 minutes. After cooling for approximately three hours to room temperature, the bomb was opened and the material removed from the pyrex flask with 50 ml. of wash water which was added to the hydrolysate. The composite was filtered and analyzed in accordance with data given in Table 1. It was observed that the humin residues in tests 1, 2 and 3 were tar-like, resinous and difficult to filter. In tests 1, 2, and 3 the hydrolysate was very dark in color, had a strong scorched odor and bitter taste. The decolorization of these hydrolysates was very difficult. The total period of heating in all of the tests of Table 1 varied from 2½ hours in test number 1 to 5 hours in test number 5. These samples gave off a considerable amount of a

TABLE 1

Hydrolysis With Water as Hydrolyzing Medium

Test	Medium	Time Hrs.	P. s. i.	Temp. ° C.	Sp. G.	Amino N/ Lb. Gluten	Approx. % Hydrolysis	pH	% Humin	Character of Humin
No. 1	Water	.5	225	190	1.0298	3.46	8.65	6.29	6.90	Tar-like
No. 2	Water	.5	310	204	1.0517	10.68	26.70	7.63	6.70	Resinous
No. 3	Water	.5	500	220	1.057	13.07	32.70	8.40	10.23	Tar-like
No. 4	Water	.5	800	225	1.0499	14.80	37.00	8.70	1.80	Granular
No. 5	Water	.5	1000	235	1.0514	17.56	43.90	8.88	1.60	Granular

gaseous product, which was shown to be carbon dioxide, by passing the gas into lime water. This indicated some decomposition of the dicarboxylic acids. The ammonia in the hydrolysate was distilled off before the amino nitrogen determinations were made.

Tests 4 and 5 had the usual hydrolysate taste and the character of the humin was much the same as the humin obtained by ordinary hydrolysis, and was granular and easily filterable. The pH of all the resulting hydrolysates were alkaline, apparently enough to aid in a slight amount of alkaline hydrolysis.

While the experiments with water as the hydrolyzing medium were not carried any further than has been indicated, there is the possibility that a longer hydrolytic period at a presure of 800 to 1000 pounds would have given a higher percent hydrolysis. It is not indicated, however, that complete hydrolysis could be obtained with water alone, or that the amino acids would have been undamaged.

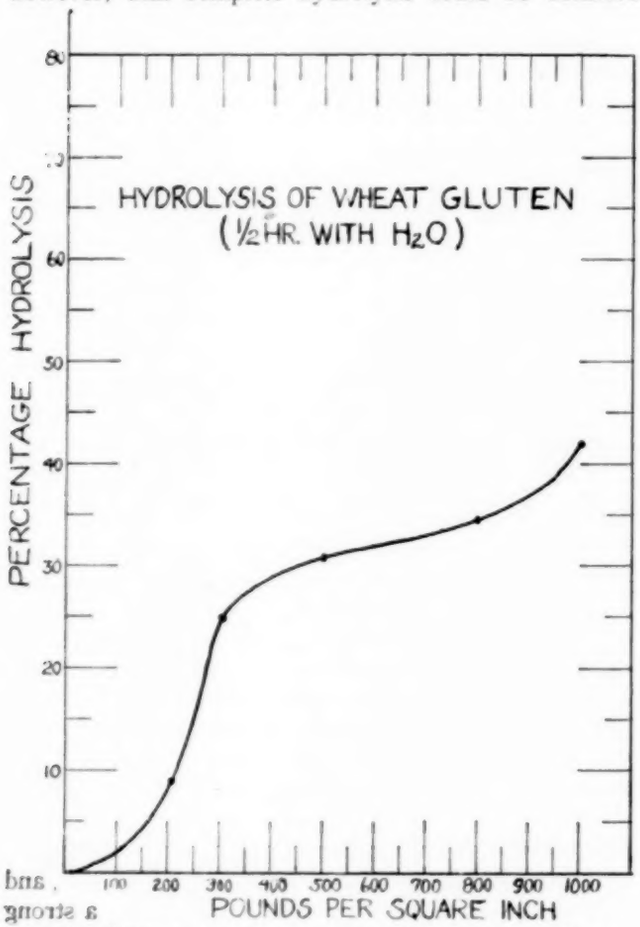


Fig. 2. Hydrolysis with water as the hydrolyzing medium.

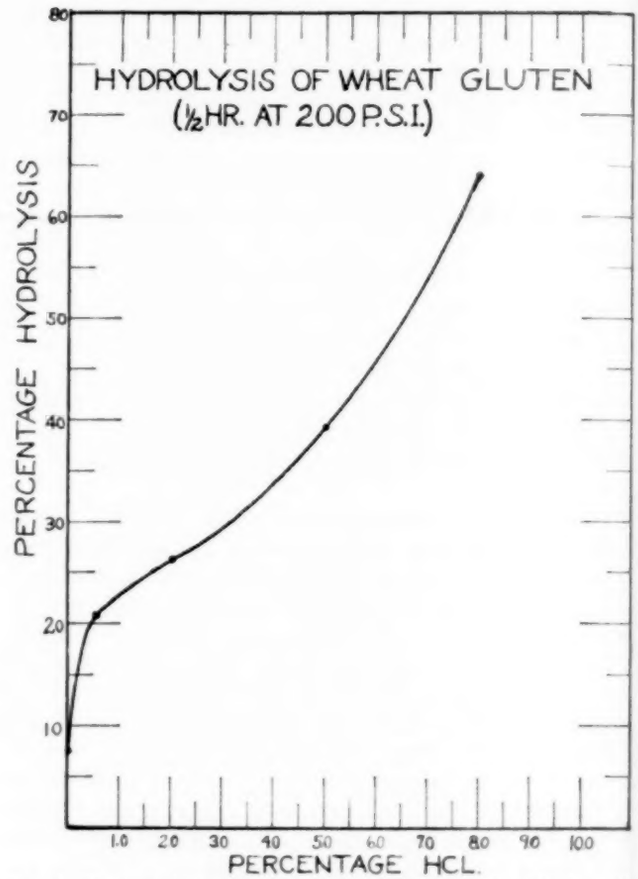


Fig. 3. Hydrolysis in different percentages of hydrochloric acid.

In Figure 2 we have expressed the results of Table 1 by plotting the percentage of hydrolysis against pressure.

Table 2 represents tests using different concentrations of HCl with varying pressures and temperatures. The addition of 1% acid lowered the pH nearer to the neutral point, and probably minimized the effect of alkaline hydrolysis. Results show that less amino nitrogen was formed with acid than was formed without acid, and that a small amount of acid of the order of 0.5% to 5% is of little value in substantially increasing hydrolysis. It is well known that HCl actually combines with some of the amino acids to form the hydrochlorides. We believe the HCl is chemically bound in this manner, and thus not able to act further as a catalyst. Because test 15 with 8% HCl gave an approximate hydrolysis

TABLE 2

Hydrolysis Under Varying Conditions of Acidity, Pressure, and Temperature

Test	Medium	Time Hrs.	P. s. i.	Temp. °C.	Sp. G.	Amino N/ Lb. Gluten	Approx. % Hydrolysis	pH	% Humin	Character of Humin
No. 6	.5% HCl	0.5	200	210	1.0455	8.8	22.00	.....	8.31	Granular
No. 7	1.0% HCl	0.5	1000	246	1.0485	14.6	36.50	.....	13.00	Granular
No. 8	1.0% HCl	2.0	950	254	1.055	12.44	31.10	.....	9.22	Tarry
No. 9	2.0% HCl	0.5	200	206	1.0522	10.59	26.50	3.88	13.67	Granular
No. 10	2.0% HCl	2.5	125	178	1.054	10.00	25.00	.....	21.00	Granular
No. 11	2.0% HCl	4.0	200	206	1.053	9.14	22.80	.....	10.00	Granular
No. 12	2.3% HCl	1.0	950	252	1.048	9.98	25.00	.....	11.09	Unreacted Protein
No. 13	5.0% HCl	0.5	200	208	1.0599	15.85	39.60	2.45	13.64	Granular
No. 14	5.0% HCl	2.0	200	206	1.0585	14.57	36.43	.....	10.00	Granular
No. 15	8.0% HCl	0.5	200	208	1.074	25.39	63.48	.....	15.40	Granular

TABLE 3

Hydrolysis in 10 Percent Hydrochloric Acid

Test	Medium	Time Hrs.	P. s. i.	Temp. ° C.	Sp. G.	Amino N/ Lb. Gluten	Approx. % Hydrolysis	% Humin	Character of Humin
No. 17	10% HCl	0 [a]	50 Max.	139	1.093	29.94	74.85	13.70	Granular
No. 18	10% HCl	0 [a]	120 Max.	172	1.086	29.63	74.08	14.60	Granular
No. 19	10% HCl	0.5	1020	252	1.058	25.57	63.94	13.00	Tarry
No. 20	10% HCl	1.0	825	239	1.068	26.55	66.38	15.00	Granular
No. 21	10% HCl	2.0	125	154	1.086	27.80	69.35	13.30	Granular
No. 22	10% HCl	2.0	500	230	1.073	26.31	65.77	14.00	Granular
No. 23	10% HCl	3.5	125	154	1.087	28.60	71.51	14.60	Granular
No. 24	10% HCl	5.0	100	146	1.086	29.70	74.24	10.60	Granular

[a] The figure 0 means that the hydrolysate was not held at the maximum, but was immediately allowed to cool.

TABLE 4

Hydrolysis in Weak Solutions of Sodium Hydroxide

Test	Medium	Time Hrs.	P. s. i.	Temp. ° C.	Sp. G.	Amino N/ Lb. Gluten	Approx. % Hydrolysis	% Humin	Character of Humin
No. 25	1.0% H_2SO_4	2.0	200	206	1.056	8.0	19.91	6.28	Tarry
No. 26	0.5% NaOH	0.5	200	206	1.056	10.59	26.47	0.46	Unreacted Prot.
No. 27	1.0% NaOH	0.5	200	206	1.063	10.17	25.40	1.41	Granular-Brown
No. 28	2.0% NaOH	0.5	200	198	1.073	9.91	24.80	4.47	Light Brown

of 63.50%, we attempted to isolate glutamic acid from this sample, according to normal procedures, in an effort to determine whether this constituent could be more readily separated. There was no free HCl present in the vacuum distillate from the hydrolysate filtrate and when the filtrate was adjusted to pH 3.2 there was a heavy precipitate which on analysis was found to be sodium chloride and glutamic acid. This was indicative that glutamic acid could be isolated from such a hydrolysate providing the degree of hydrolysis was sufficiently high.

In Figure 3 is shown graphically the approximate hydrolysis from results given in Table 2.

Increased amounts of HCl were used at varying pressures and temperatures, and while it was noted that the maximum amino nitrogen is much lower than the expected theoretical value, it is obvious that the increased acid assists tremendously in the hydrolysis of the protein. The appearance, smell and taste of the various test samples indicated that there had been some destruction of the protein prior to hydrolysis, particularly in tests 19 and 20 where very high pressures and high temperatures prevailed. In test 20 the hydrolysate was further hydrolyzed with acid, representing a total acid concentration of 14% HCl to determine if the nitrogen which was unaccounted for could be released as amino nitrogen. An additional six-hour hydrolysis by refluxing at 113° C. gave an increase in hydrolysis from 66.38% to 88.37%.

Regular procedures for the separation of glutamic acid were used and a yield representing 40% of the expected glutamic acid was obtained. It is apparent that the protein had been altered in some manner, prior to hydrolysis, and that the glutamic acid separation had been impaired. This again indicates that protein damage occurs at high pressures and temperatures. It was interesting to find that excellent hydrolysis was obtained with 10% HCl as in tests 17 and 18, but it is strongly apparent that sufficient acid must be present to form the acid salts of all of the amino acids present in the protein before complete or nearly complete hydrolysis can be obtained.

Thus far, these studies have indicated that temperature and pressure together, or pressure alone, will not hydrolyze proteins unless the acid requirement is met. High temperatures actually destroy, or partially destroy the protein molecule, rather than hydrolyze it.

In tests 17 and 18 the hydrolytic reaction occurred at fairly low pressures, but much higher than have been commercially considered. It is interesting to observe that the approximate degree of hydrolysis is relatively high, and yet the acid is no stronger than in the other tests. This would seem to indicate that more efficient hydrolysis can be obtained at a lower pressure.

In attempting to obtain a more complete picture concerning the effects of high pressures of proteins with different catalysts, test No. 25 with 1% sulphuric acid was made. The results were not sufficiently encouraging to continue work with this acid, and, in our opinion, were not comparable with the same strength HCl. It was not thought desirable to go to higher pressures than 200 lbs. per square inch because of previous results which indicated protein destruction.

Also in Table 4 we have shown the results obtained in three tests with weak solutions of sodium hydroxide. These were not satisfactory even though the amount of hydrolysis compared favorably with that obtained with comparable amounts of HCl. It is known that sodium hydroxide destroys some of the amino acids and racemizes certain others. Also noted in these three tests was the unusual amount of ammonia liberated.

TABLE 5

Rate of Hydrolysis Under Usual Commercial Conditions

Test	Medium	Time Hrs.	Temp. ° C.	Amino N/ Lb. Gluten	Approx. % [a] Hydrolysis
No. 1	20% HCl	8	108-110	35.8	89.50
No. 2	20% HCl	9	108-110	38.5	96.25
No. 3	20% HCl	11	108-110	39.8	99.50

[a] Complete hydrolysis of wheat gluten (85% protein) gives 40 grams Amino N/lb. gluten.

In Table 5 data is given to show the effect of time upon the percent of hydrolysis of the same gluten at the ordinary temperature and pressure used for the commercial production of hydrolysates with 20% HCl. Almost complete hydrolysis can be obtained in eleven hours at temperatures of 108-110° C.

Discussion

The odor and appearance of the hydrolysate in tests 17 and 18 in Table 3 were very comparable to hydrolysates obtained by current hydrolysis practices, and it is thus logical to assume that the protein has not been adversely affected or destroyed prior to hydrolysis by this treatment. It is our concept that some pressure between 50 and 100 pounds is indicated as optimum where maximum hydrolysis can be obtained without protein destruction. For these pressures to be practical commercially, the hydrolysis time would necessarily have to be considerably less than by the present reflux treatment.

Further preliminary tests have indicated 75 to 80 pounds pressure is about the maximum that can be used without destruction of protein, and it has also been indicated that the maximum acid requirement for such a procedure would be from 16 to 17% HCl. We have determined that complete hydrolysis can be obtained by refluxing the protein with 18% to 19% HCl in a period of 15 hours. Therefore, it is reasonable to suppose it would be practical to hydrolyze under a pressure of 75 lbs. with 16% HCl and that complete hydrolysis could thus be obtained.

There is the real possibility that the hydrolysis of wheat gluten and related protein materials could be hydrolyzed by making a slurry of the protein in an acid of appropriate concentration, and that this slurry could be passed through a heated tube to bring about hydrolysis. Perhaps the slurry could be forced through by gravity or perhaps some type of screw mechanism could be devised to keep the slurry moving at a predetermined speed through the heated pressure tube. The advantage of the flow method over the static method is that very little time would be required for heating and cooling. Hence the time of contact in the hot zone would be under much better control. Probably such a continuous system could be devised which would, to some extent, revolutionize the production of protein hydrolysates.[b]

Summary

We have indicated the possibilities of improving the hydrolytic reactions of proteins with high pressures and temperatures, and it is our belief that several opportunities exist for improving the production of protein hydrolysates with moderate amounts of pressure, such as 75 to 80 pounds per square inch, and at temperatures up to 180° C. by a continuous system in a relatively short time whereby hydrolysis can be effected without previous alteration or destruction of the protein substances.

Since the experiments which I have described could have been much more exhaustive, it is clearly evident more work can be done on this problem, particularly from the theoretical standpoint, to uncover valuable information. I believe there are definite indications these more thorough fundamental studies could change our present concepts and knowledge concerning protein hydrolytic processes and be further translated into improved industrial procedures and products.

[b] Unpublished information has been presented to the author indicating that a continuous system for the hydrolysis of proteins is in commercial operation.

Acknowledgment

The author acknowledges the assistance of Dr. Charles D. Hurd and Mr. George Bernard of Northwestern University, for the use and supervision of the pressure equipment and tests made with same, and, to Mr. Robert M. Stephenson[c] and other associates of the Griffith Laboratories for analytical data.

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[c] Now with Basic Vegetable Products Co., Vacaville, California.

The Influence of Heat-Processing on the Functional and Nutritive Properties of Protein[a]

DANIEL MELNICK[b] AND BERNARD L. OSER[c]

The concept of food protein as N x 6.25 should be extended to include a consideration of both the functional and nutritive properties of the protein. The functional properties may be evaluated by the use of standardized procedures for determining the degree of protein denaturation; the nutritive properties, by determining the amino acid composition of the protein and its susceptibility to enzymic digestion. For optimal utilization of food proteins all essential amino acids must not only be available for absorption but must also be liberated during digestion in vivo at rates permitting effective mutual supplementation.

Since the major portion of this report deals with the susceptibility of protein to enzymic digestion as a factor in nutrition, the title of this paper might have been "The Influence of Heat-Processing of Protein on the Availability of the Amino Acids" in keeping with the subject of this symposium. However, the functional properties of protein, also readily modified by heat-processing, affect appearance and palatability of the end-product and therefore cannot be dissociated from the nutritive properties of the protein. Food must be consumed in order to make its nutrient contribution.

It is not uncommon for a given food material to be processed in different ways without a change in its protein content or in the amino acid composition of the protein complex; yet these foods cannot be used interchangeably without modifying the quality of the end-product. Many food technologists, aware of the limitations of their raw materials, usually strive to attain food formulations which give optimal performance, the functional properties of the protein receiving primary, if not exclusive, consideration. On the other hand, the nutritionist concerns himself with the influence of processing on the nutritive value of the protein, striving to avoid destruction of the essential amino acids and to attain a product free from factors which might interfere with the availability of the amino acids. Ease of manufacture, appearance, palatability, stability, and ready utilization of the end-product, however, are important considerations and cannot be sacrificed even for optimal nutritive value. The ultimate aim, of course, should be to obtain a food or a blend of food materials in which both functional and nutritive properties of the protein are at a maximum. However, this can be realized only in a few instances.

The experience of manufacturers of soy products will serve as an excellent illustration of the problem to be presented. Soy flour is used principally as (a) a wheat flour extender, (b) as a source of "tofu," an oriental main dish prepared by forming a curd from the water-extractable soybean protein, and (c) as a major ingredient in low-cost food preparations such as soup mixes. For the first two purposes it is essential that the protein in the product be in an undenatured form so that the functional (utility) properties will be unimpaired. However, in those food products consumed after minimal heating at atmospheric pressure and in which the functional properties of the protein are not critical, the soy product should be adequately processed to increase the biological value of the protein to a maximum. In raw or insufficiently heat-processed soy products an anti-tryptic factor is present *(8, 28)* which interferes with the digestibility of the soy protein; excessive heat-processing effects a reduction in the nutritive value of the protein *(79, 62, 10, 20, 25)*. The soy industry has been aware of this situation and has attempted to manufacture products under standardized conditions to serve specific functions. A soy flour intended for use in bread may not be satisfactory for inclusion in a soup mix and vice versa. The group at the Quartermaster Food and Container Institute has prepared a specification for the procurement of soy products which unfortunately fails to recognize these differences. Simple objective test methods are not available at the present time for inclusion in a specification to justify setting specific requirements for the two kinds of soy flour desired; namely, for baking bread and curd formation, or for soups, nährmittel, etc. A collaborative research project with the soy industry is now under way for the purpose of incorporating in the specifications suitable methods of test to insure that flour required for a specific purpose is procured. Too frequently have reports been received from overseas areas severely criticising the soy products furnished. Heat-processed soy meal containing practically no water-extractable protein has been furnished to the civilian populace in the Orient, whereas low heat-processed soy flours have been shipped to Germany for inclusion in soup mixes and food combinations which are consumed either as such or after minimal heating.

The Functional Properties of Protein in Food Materials

In Table 1 are shown five food products subjected to heat-processing with the view toward obtaining products whose protein components exhibit desirable functional

[a] This paper from the Quartermaster Food and Container Institute for the Armed Forces, as one of the participating laboratories, has been assigned Number 189 in the series of papers approved for publication. The paper was presented by the senior author in a symposium on "Amino Acids" before the Institute of Food Technologists, Eighth Annual Convention, Philadelphia, Pa., June 9, 1948. The views or conclusions contained in this report are those of the authors. They are not to be construed as necesssarily reflecting the views or indorsement of the Department of the Army.

[b] Quartermaster Food and Container Institute for the Armed Forces, Chicago, Ill. The experimental work on the nutritive properties of proteins was carried out while the senior author was associated with Food Research Laboratories, Inc., Long Island City, N. Y. Certain phases of this work have been reported elsewhere *(60b, 52, 61)*. Studies on both the functional and nutritive properties of proteins are continuing at the Quartermaster Food and Container Institute for the Armed Forces.

[c] Food Research Laboratories, Inc., Long Island City, N. Y.

TABLE 1

Influence of Heat Processing on the Functional Properties of Protein

Protein Source	Heat Processing	Resulting Product
Soybean	100°-135° C. for 10-0.1 min.	Slightly denatured protein (50-65% extractable) enzyme (diastase and lipoxidase) inactivated; used for curd formation in main dish preparations, in bread manufacture, in sausages, and in alimentary pastes.
Egg	Preheated to 60° C., spray drying to 2.0% moisture content, temperature <65° C.	Slightly denatured protein; used to form a coagulum in main dish preparations, for imparting proper body and structure to baked products, spaghetti, etc., for emulsifying properties.
Yeast	28-30° C. to 8% moisture content.	Enzymes in intact cells still active; used as a fermentation agent in baking industry.
Flour	55-80° C. for approx. 1 min.	Accelerated maturation, replacing agene process, with the result that concentration of free sulfhydril compounds is reduced without impairment of the diastatic activity; used in baking industry.
Milk	90-92° C., 15 min.	Denatured protein, enzymes inactivated, low in volatile sulfhydril groups; used in bread manufacture.
	70-72° C., 15 sec.	Slightly denatured protein, which redissolves in preparing beverage.
	61-62° C., 30 min.	Slightly denatured protein in frozen pasteurized milk.

properties. Additional materials could have been included, but those listed will suffice for this discussion. Excessive heat-processing (or minimal heating in the case of the milk powder employed for baking purposes) alters the character of the products to such an extent that they can no longer be employed for the purposes intended.

Rather than depend solely upon subjective utility tests for rating food materials in which the functional properties of the protein are susceptible to change during processing, it is suggested that precise, objective tests of the extent of protein denaturation be employed. Of course, in each case correlation between the utility and biochemical tests has to be established. Various laboratory procedures for ascertaining the degree of protein denaturation are already being employed in the laboratories of the food industries. Thus in the case of soy and egg protein, measurements of the solubility index are usually made. The results of these tests characterize the functional properties of the product at the time the material is freshly prepared; these, however, do not reflect the potentialities of the protein to undergo further changes during the subsequent storage periods, with a resulting decrease in solubility. It would seem desirable to supplement the solubility measurement with tests to ascertain whether or not the salting-out characteristics of the protein have been altered. Denaturation of coagulable protein can occur without precipitation *(51)*. Since the salting-out characteristics of proteins change under conditions inducing incipient denaturation, a quantitative salting-out test should serve as a better indicator of the actual degree of denaturation effected, than the simple solubility measurement, and of the tendency of the protein to become insoluble during prolonged storage. Harland and Ashworth *(29)* have used the salting-out behavior of the whey protein in dried milk for purposes of classifying dried skim milk samples with respect to baking qualities. In this case protein denaturation is desired. At the Institute a precise objective protein precipitation technique has been evolved for rating the potentialities of soy preparations for curd formation. This same procedure may prove to be useful in rating soy flours for use in bread manufacture.

Influence of Heat-Processing on the Nutritive Value of the Protein

The above title constitutes the major theme of this discussion. Three factors, broadly speaking, determine the nutritive value of a food as a source of protein. These are (a) the quantity of protein expressed in terms of total solids content, (b) the essential amino acid composition of the protein, and (c) the availability of the amino acids for tissue protein synthesis.

It is incorrect to compare two food products on the basis of their protein content alone without reference to their total solids content. Reference is sometimes made to the protein value of a cereal or leguminous food relative to that of meat. In terms of total solids, materials like oats or soybeans furnish much less protein than meat, even though their net protein content may be the same or even greater.

The chief consideration in the selection of dietary proteins is their content of indispensable amino acids, since proteins can be no better than the biological sum of their amino acids. Animal proteins have greater biological value than vegetable proteins because they contain a greater number of essential amino acids in quantities of nutritional significance. The essential amino acids, however, must not only be present but must be readily available for absorption and utilization by the animal organism.

Papers have appeared demonstrating with a number of species that the protein in properly heat-processed soy products has a much higher biological value than that of the raw bean *(60, 55, 34, 35, 79, 33, 62, 32, 2, 15, 54, 20, 25, 46, 77)*. Supplementation with methionine eliminates in large part the discrepancy between the two products *(32, 2, 54, 20, 11, 68)*. In addition to soybeans, many other leguminous proteins seem to improve in nutritive value after the application of heat *(38, 75, 22, 76, 23, 21, 67)*. On the other hand, excessive heating has been shown to impair the biological value of proteins. The adverse effects of heat on milk proteins (particularly casein) *(56, 27)*, on edestin *(73)*, on blood globin *(14)*, and on the proteins in cereals *(56, 44, 58, 71, 43, 64)*, meat *(57, 69, 30)*, and fish products *(50, 66, 78)*, in soybean *(79, 62, 10, 20, 25)*, and other legumes *(83, 21, 59, 67)*, in coconut

meal *(54)*, and in a baking formulation *(6)* have been reported. In practically every case supplementation of the ration with lysine effected substantial if not complete correction of the nutritional deficiency.

Storage of foods over extended periods of time appears to cause impairment in the nutritive value of the protein similar to that noted following excessive heat-processing. This has been observed in studies with dried skim milk *(36)*, with soy meal *(41)*, and with the cereal grains *(41, 42, 40)*.

Throughout the papers indicated above, data are presented demonstrating that heat-processing of foods has a profound effect on the nutritive value of the protein without affecting the protein content, the essential amino acid composition, or the degree of protein digestibility *in vivo*. Despite the fact that methionine is the principal limiting amino acid in raw foods, whose protein value can be improved by heat-processing, and that lysine plays a corresponding role in the case of excessively heated proteins, the contents of these amino acids are not materially affected by the processing techniques. This had led to the conclusion that these amino acids in the ineffective proteins are not biologically available *(84, 17, 7)*. In the case of lysine it has been postulated *(17, 7)* that a new peptide linkage forms as a result of heat-processing involving the ϵ-amino group of lysine and the free carboxyl group of a dicarboxylic amino acid and that this complex is resistant to enzymic digestion.

In the present report data will be presented demonstrating with heat-processed proteins that the *rate* of enzymic liberation of the amino acids, rather than *degree* of amino acid availability, is of critical importance in determining the efficiency with which the absorbed amino acids are retained for tissue protein synthesis. In studies of amino acid supplementation of deficient amino acid mixtures *(18, 26, 9)* or of an inadequate ration *(4)*, or of proteins supplementing each other *(37)*, time intervals have proved to be exceedingly important; as the time interval between feeding the dietary components is reduced more effective biological responses are obtained. As a working hypothesis in the present studies, it has been postulated that for optimal utilization of protein all essential amino acids must not only be available for absorption but must be liberated during digestion *in vivo* at rates permitting mutual supplementation, and that heat-processing influences the relative rate of liberation of the amino acids. That amino acids are liberated during digestion at different rates has previously been reported *(53)*, but the nutritional implications of such observations have been largely neglected. Other factors, such as the presence in foods of naturally occurring toxic agents *(45)*, vitamin-amino acid interrelationships *(53b)*, or the necessity for the animal organism to absorb amino acids in certain peptide linkages *(80, 81, 82)* undoubtedly also play an important role in protein and amino acid utilization.

In the early phases of the present investigations it became apparent that there would be need for a simple *in vitro* technique for estimating the susceptibility of protein, before and after heat-processing, to enzymic digestion. In this report are presented the *in vitro* digestibility method selected, the details and reliability of the improved formol titration procedure used in the *in vitro* studies, the variables requiring control in the application of the *in vitro* procedure to the determination of the susceptibility of protein to enzymic digestion, the results of the *in vitro* studies of the influence of heat-processing on protein digestibility, and the correlation of the *in vitro* findings with the results of biological and microbiological studies.

Experimental Part

Various methods are available for biological determination of the nutritional value of protein. The preferred technique is undoubtedly the nitrogen balance method of Mitchell and his associates *(53)*. The procedure affords a measure of the retention of absorbed nitrogen for tissue protein synthesis (the biological value of the protein) and at the same time gives a specific value for the percent of the dietary nitrogen that is absorbed (the degree or coefficient of protein digestibility). That the precision of the assay technique is excellent is indicated by the ease with which reproducibility can be held within $\pm$ 5 percent. However, the procedure demonstrates but does not explain why the same protein after various methods of processing shows differences in biological value even though the amino acid composition and coefficient of digestibility remain unchanged. It will be shown in this report that by supplementing the bioassay technique with an *in vitro* digestibility procedure, the probable basis for this phenomenon may be elucidated. Indeed, the method for determining the *in vitro* digestibility of a given food material, after correlation has been obtained with the bioassay has practical value in plant control of processing methods affecting the nutritional quality of the protein since it obviates the need for confirmatory bioassays.

The in vitro Digestibility Technique

The details of the *in vitro* technique for estimating susceptibility of proteins to enzymic digestion are presented in Figure 1.

A suspension or solution of the material containing six

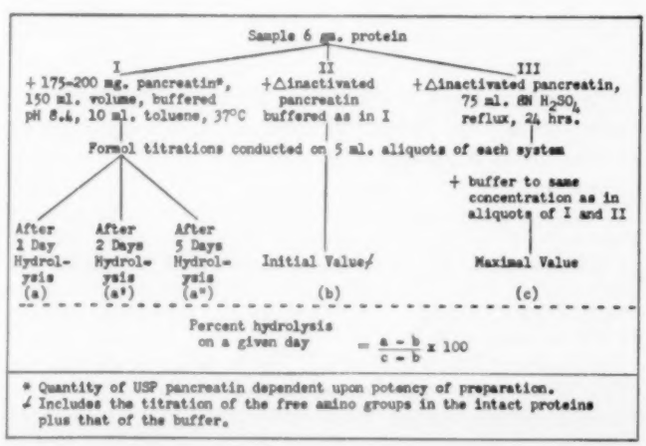

Sample 6 gm. protein
I
II
III
+ 175-200 mg. pancreatin*, 150 ml. volume, buffered pH 8.4, 10 ml. toluene, 37°C
+△inactivated pancreatin buffered as in I
+△inactivated pancreatin, 75 ml. 6N H_2SO_4, reflux, 24 hrs.
Formol titrations conducted on 5 ml. aliquots of each system
+ buffer to same concentration as in aliquots of I and II
After 1 Day Hydrolysis (a)
After 2 Days Hydrolysis (a')
After 5 Days Hydrolysis (a'')
Initial Value/ (b)
Maximal Value (c)
Percent hydrolysis on a given day = $\frac{a-b}{c-b} \times 100$
* Quantity of USP pancreatin dependent upon potency of preparation.
/ Includes the titration of the free amino groups in the intact proteins plus that of the buffer.

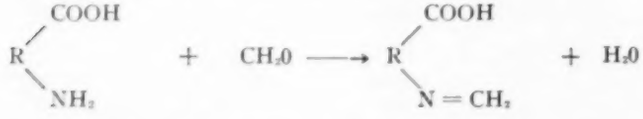
FIG. 1. *In vitro* technique for estimating susceptibility of proteins to enzymic digestion.

grams of protein is buffered [d] to pH 8.4, 175 to 200 mg. of USP pancreatin added, and the volume brought to 150 ml. Ten ml. of toluene are introduced and the mixture incubated at 37° C. Periodic formol titrations are conducted on 5 ml. aliquots of the enzymic digests. To another sample of the protein-bearing material, similarly buffered and diluted, is added the heat-inactivated pancreatin and an aliquot then taken for the formol titration. To a third sample of the test material, the sulfuric acid is added, and the suspension refluxed for 24 hours. A 5 ml. aliquot is taken, buffer added to the same concentration as in aliquots of I and II, and the material then analyzed by formol titration. In the case of III, the maximal titration value is obtained, representing ultimate hydrolysis to the amino acid stage. Thus (a — b), the increase of free amino nitrogen on a given day, over (c — b), the theoretical value for liberated amino nitrogen in a completely hydrolyzed sample, times 100 gives the percent hydrolysis of the protein. (It has proved desirable in many instances to determine the percent hydrolysis attained at intervals during the first 24-hour period). The use of sub-optimal quantities of the pancreatin permits digestion to proceed for several days at 37° C., slowing down the rate of liberation of the amino acids to such an extent that differences in digestibility of proteins may be detected. In materials containing readily digestible protein, hydrolysis is deliberately limited to approximately 50 percent. Obviously, this system does not duplicate conditions in the gastrointestinal tract. However, it constitutes a simple method for use as a routine laboratory control measure of the relative digestibility of the protein in materials undergoing heat-processing. Correlation of this simplified procedure with the results of animal assays to be presented in this report has amply justified the empirical conditions of the test.

The validity of the *in vitro* technique for determining protein susceptibility to enzymic digestion leans heavily on the reliability of the formol titration procedure.

The Formol Titration Procedure and Its Reliability

The oldest and simplest formulation [e] of the reaction between amino acids and formaldehyde is as follows:



As a result of the reaction the basic properties of the amino group are destroyed, permitting direct titration of the carboxyl group.

[d] The test material is suspended or dissolved in 60 ml. of a phosphate buffer solution (250 ml. of M/5 KH_2PO_4 plus 240 ml. of M/5 NaOH, diluted to 1000 ml. volume; pH 8.4), and the pH readjusted to 8.4, if necessary. Ten ml. of the buffer solution containing the pancreatin are then added and the volume brought to 150 ml. mark with water.

[e] The formation of monomeric Schiff bases in the case of aliphatic compounds may be questionable; compounds with the chemical composition of Schiff bases are more likely cyclic trimers. For an informative discussion of the reaction of formaldehyde with amino acids and proteins, reference is made to the excellent review article by French and Edsall *(24)*.

In carrying out the formol titration, the test solution, containing approximately 30 mg. of nitrogen, is first adjusted to pH 7.0 in a total volume of 20 ml. Two ml. of a 37 percent solution of formaldehyde, adjusted to pH 7.0, are added. This causes a decrease in the pH of the solution in most cases between 5.0 and 6.0. The solution is then titrated to pH 9.5 with standard 0.1N sodium hydroxide. The formol titration as usually described is based on the use of a visual end-point, phenolphthalein being employed as the indicator. In the present procedure all pH measurements are made with the Beckman pH meter, using the glass electrode. Whereas the methods employed in the literature, almost without exception, terminate the formol titration at pH 8 to 9, it is specified here that the test solutions be titrated to pH 9.5.

The justification for this change in the procedure is evident from the titration curves in Figure 2. Here are plotted the percent of total nitrogen titrated at a given pH following the addition of the formaldehyde. It may be noted that at pH 9.5 the formol titratable nitrogen values equal the Kjeldahl nitrogen figures for ammonium chloride, for valine (a typical monoamino-monocarboxylic acid), and for glutamic acid (a typical monoamino-dicarboxylic amino acid). In the case of glutamic acid the adjustment of the solution to pH 7 neutralizes one carboxyl group so that subsequent titration, following the addition of formaldehyde, is similar to that for the monoamino-monocarboxylic acid. In the case of tryptophane and the basic amino acids (each of the latter as the hydrochloride), the formol titratable nitrogen values are lower. In valine there is one nitrogen per carboxyl group; in the others there is more than one nitrogen per carboxyl group. Thus for tryptophane containing two nitrogens the value calculated from the formol titration is found to be exactly one-half of the total Kjeldahl nitrogen; for arginine containing four nitrogens per carboxyl group the nitrogen by formol titration is exactly one-fourth; histidine with three nitrogens per carboxyl group gives a formol titratable nitrogen value 35 percent of the total nitrogen figure. On the other hand, lysine with two nitrogens gives a value 90 percent of the Kjeldahl value. Apparently in the case of lysine the hydrochloride group still remains attached to one of the amino groups when the solution is brought to pH 7, and this as well as the carboxyl group is titrated following reaction of formaldehyde with the amino groups. The basicity of the guanidine group in arginine is probably so great that the bound hydrochloric acid is not released following neutralization to pH 7.0, addition of the formaldehyde and subsequent titration. In the case of histidine, having an isoelectric point very much closer to that of the monoamino-monocarboxylic acids than that of either lysine or arginine, little hydrochloric acid remains bound after the pH adjustment to 7.0 to complicate the formol titration. In titrating the other amino acids selected, some discrepancies between formol titratable and total nitrogen values are found but these are not excessive.

It is apparent from the results obtained that if the titrations were terminated at pH 8 or 9, appreciably

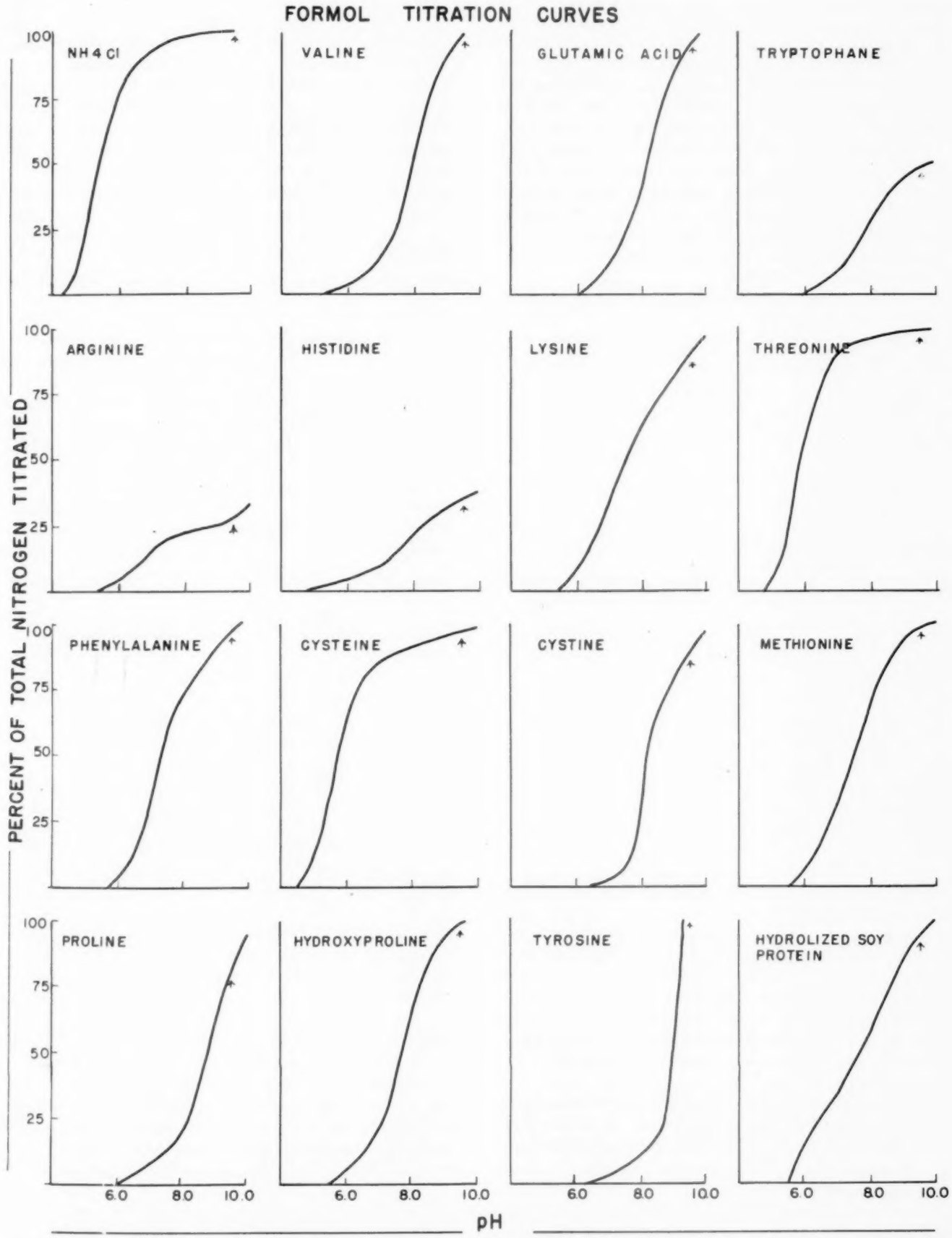


FIG. 2. Relation of formol titratable nitrogen figures at different pH values to total nitrogen content. (The arrows point to pH 9.5.)

greater deviations from the total nitrogen values would have been obtained. The data with the soy meal protein are of interest. They indicate how the formol titration works in actual practice. It will be noted that 94 percent of the total nitrogen is measurable by formol titration. This should be expected according to the following reasoning: The total lysine, arginine, histidine, and tryptophane content of most proteins varies between 10 and 20 percent; in soy protein they total about 14 percent. The formol titration as described actually measures somewhat more than one-half of the total nitrogen of these amino acids. Thus, 86 plus 7 or 93 percent of the theoretical value should have been obtained on titrating this protein hydrolysate.

Further justification for selecting pH 9.5 as the end-point of the formol titration may be derived from the data listed in Table 2. Eighteen food products were subjected to Kjeldahl analysis and to formol titration according to the procedure described. The deviation of the formol titratable nitrogen from the Kjeldahl nitrogen is indicated in the last column. It will be noted that nitrogen by formol titration tends to be lower than by Kjeldahl anaylsis, being on the average about 4 percent less. From the titration curves presented in Figure 2, it is apparent that this could have been predicted.

TABLE 2

Justification for Selecting pH 9.5 As the End Point for the Formol Titration

Sample	Nitrogen Content		
	Kjeldahl Analysis (a)	Formol Titration* (b)	Deviation†
	percent	*percent*	*percent*
Raw Soy Meal	6.00	5.63	— 6.1
Expeller Processed Soy Meal	7.39	6.80	— 8.0
Solvent Processed Soy Flour	8.43	7.71	— 8.5
Dried Skim Milk	5.45	5.62	+ 3.2
Whole Milk	0.55	0.53	— 6.8
Casein	14.36	13.47	— 6.1
Whole Egg	1.92	1.89	— 1.7
Yeast Powder	7.40	7.40	0.0
Rice Bran Concentrate	1.41	1.41	0.0
Whole Oats	1.94	1.98	+ 2.5
Dehulled Cooked Oats	2.54	2.62	+ 3.1
Defatted Sunflower Meal	8.24	7.46	— 9.4
Whole Wheat	2.61	2.70	+ 3.4
Defatted Wheat Germ	5.54	4.67	— 15.6
Beef Steak	3.32	3.12	— 6.3
Chicken Product	2.40	2.46	+ 2.6
Liver Product	2.19	1.98	— 9.5
Whole Beef Blood	2.88	2.80	— 2.8
Average			— 3.6

*Of acid hydrolyzed sample.

† $\frac{b - a}{a} \times 100$.

The Control of Variables in the Application of the *in vitro* Procedure to the Determination of the Susceptibility of Proteins to Enzymic Digestion

Obviously the rate and degree of proteolysis should be dependent upon the activity of the pancreatin. In Table 3 are presented the results of tests of three soy meals and of Labco casein with fresh USP pancreatin and with a preparation which had been stored two years at 5° C. These two preparations had originally given the same formol titration values for the same test samples. It will be noted that in the case of soy meals the rate of hydrolysis is affected by the activity of the pancreatin, but only after the first day of hydrolysis. However, the relative ratings of the samples are not affected by the pancreatin employed. In any extended series of studies where it might be desirable to compare the degree of susceptibility of protein to enzymic hydrolysis, it is essential that the activity of the enzyme preparation be eliminated as a variable. This can be accomplished by standardizing each new batch of pancreatin to allow use of equivalent weights of the preparation. On the basis of the results presented here, it was decided not to employ casein as the substrate for the standardizations. Casein is so readily digestible that smaller quantities of enzyme failed to influence its rate of digestibility to the same extent as in the case of some other test materials stored in an hermetically sealed container at 0° C. A heat-processed soy meal is preferred for standardizing each batch of enzyme material.

If possible, the protein substrate subjected to the *in vitro* test for digestibility should be treated to render inactive any proteolytic enzymes that may be present. This is apparent from the illustrative data in Table 4 on raw soy meal, heat-processed soy meal, and casein. The latter was included because of the report by Warner and Polis *(74)* which claimed that all commercial casein preparations contain proteolytic enzymes. It will be noted that in the case of the raw soy, incubation of the material without the pancreatin gave rise to formol-titratable nitrogen. However, the proteolysis due to the enzymes naturally present and that due to the added pancreatin are not additive but synergistic. Thus the results of the digestitbility tests of the fat-extracted, enzyme-inactivated raw soy with added pancreatin gave values much less than would be obtained by subtracting the result of Experiment 2 from that of Experiment 1. Heat-processed soy, of course, is enzymically inactive. The tests have demonstrated no significant proteolysis of casein (Labco vitamin-free casein) incubated under the conditions described. From the data for raw soy meal it is obvious that erroneous results may be obtained for protein digestibility if the naturally present enzymes are not previously inactivated.

Pancreatin also contains a lipase capable of releasing free fatty acids which are neutralized at a pH above 7.0. Thus if a significant amount of free fatty acids were liberated in a digestion mixture, the neutralization of the

TABLE 3

*Rate and Degree of Proteolysis Dependent Upon Activity of Pancreatin**

Pancreatin	Test Sample	Degree of Hydrolysis of the Proteins		
		After 1 Day	After 2 Days	After 5 Days
		percent	*percent*	*percent*
Fresh Preparation	Soy Meal No. 1	8	15	18
	Soy Meal No. 2	12	19	28
	Soy Meal No. 3	12	19	33
	Casein	19	32	43
Stored 2 Years at 5° C.‡	Soy Meal No. 1	9	10	13
	Soy Meal No. 2	12	14	17
	Soy Meal No. 3	10	14	21
	Casein	20	31	37

*For each experiment 200 mg. of USP pancreatin was employed.

‡ Sample had been used repeatedly during this holding period, involving frequent removals from the refrigerator and exposure to the atmosphere.

TABLE 4

Influence of Naturally Occurring Proteolytic Enzymes on the In Vitro Test of Protein Digestibility

Sample (Protein Content)	Experiment		Hydrolysis of Proteins		
	No.	Description	After 1 Day	After 2 Days	After 5 Days
			percent	*percent*	*percent*
Raw Soy Meal* (38.3%)	1	Incubated with pancreatin	24	29	37
	2	Incubated without pancreatin	0	4	9
	3	Fat extracted, inactivation of enzyme at 100° C., then incubated with pancreatin	10	16	21
	4	Same as 3, but without pancreatin	0	0	0
Processed Soy Meal (49.0%)	5	Incubated with pancreatin	14	25	37
	6	Incubated without pancreatin	0	0	0
Casein (91.6%)	7	Incubated with pancreatin	19	32	43
	8	Incubated without pancreatin	0	0	0

*Digested samples subjected to ether extraction prior to formol titrations.

TABLE 5

Influence of Fat in Test Sample on the In Vitro Test of Protein Digestibility

Sample	Composition		Test	Enzymic Hydrolysis of Proteins			F. T. N.† in Acid Hydrolyzed Sample
	Protein	Fat		After 1 Day	After 2 Days	After 5 Days	
	percent	*percent*		*percent*	*percent*	*percent*	*% Kjeldahl Value*
Whole Milk	3.50	4.0	Direct	16	21	25	113
			Defatted*	20	25	28	93
Hard Boiled Egg	12.0	11.5	Direct	10	13	29	103
			Defatted*	10	14	31	98
Raw Soy Meal	38.3	21.8	Direct	9	16	20	100
			Defatted*	10	16	21	91
Expeller Processed Soy Meal	49.0	1.6	Direct	14	25	37	91
			Defatted*	14	25	37	91

* Enzymic and acid digests adjusted to pH 1, extracted with ether (residual solvent evaporated off), and then subjected to formol titrations.
† "Formol titratable nitrogen."

fatty acids might lead to erroneously high formol titration values. The significance of the fat in the test sample on the *in vitro* test of protein digestibility is presented in Table 5. The ratio of protein to fat may be calculated from the data in columns 2 and 3. When the amount of fat relative to protein is large, such as in egg or whole milk, an error may be introduced in the formol titration. The actual titration figures demonstrated that during *acid* hydrolysis of the protein-bearing materials, the fat is readily converted to free fatty acids which are then titrated. However, only negligible amounts of fat are hydrolyzed by the pancreatin under the conditions of the test, so that the formol titration values on the samples before and after ether extraction remain essentially the same. Because of the increase in apparent formol-titratable nitrogen in the acid-hydrolyzed samples, and therefore in the denominator in the fraction expressing degree of proteolysis, there appears to be a decrease in protein digestibility during enzymic digestion of samples containing a large proportion of fat. In products with approximately one-half as much fat as protein, for example the raw soy meal, no appreciable error is introduced by use of the direct formol titration. A factor responsible for the smaller-than-expected degree of interference of the fatty acids in this series is the rapidity with which formol titrations are routinely carried out. The fatty acids are insoluble in water and only by neutralization with sodium hydroxide are they brought into the aqueous phase. This involves stirring and delay after each addition of alkali. In the present series, the titration values were obtained with the same timing required for conducting formol titrations on samples free of fat, that is, about five minutes for the titration. Because of the results obtained in this series of tests, it is now the practice to defat all digestion mixtures in which the fat content exceeds half the content of protein.

Some plant proteins contain considerable amounts of amide nitrogen. In Figure 2 it was demonstrated that ammonia reacts like a free amino group in the formol titration. Amide nitrogen, on the other hand, fails to influence the titration values. However, in the acid hydrolysis of the protein for the theoretical maximum formol titration, amide nitrogen is converted to ammonia. The possibility therefore existed that some error might be introduced unless correction is made for ammonia derived from this source. This was investigated and the results are presented in Table 6. Ammonia was determined by adjusting the pH of the suspension to 12.0 and vacuum-distilling the ammonia at 35 to 40° C. into solutions containing a known volume of standard acid. It will be noted that there was no difference in the rate or degree of hydroylsis of the protein as a result of free ammonia in the digest, the figures with and without corrections for ammonia being essentially the same. This is explained by the fact that during enzymic hydrolysis of the protein, ammonia was liberated at almost the same rate as the amino groups. Thus,

TABLE 6

Influence of Ammonia Derived from Amide Nitrogen on the In Vitro Test of Protein Digestibility

Sample (Protein Content)	Amide Nitrogen	Test	Hydrolysis of Proteins		
			After 1 Day	After 2 Days	After 5 Days
	% of total N		*percent*	*percent*	*percent*
Defatted Sunflower Meal (52.5%)	17	Direct	16	25	37
		Correcting for NH_3 in sples.	17	28	34
Yeast Powder (46.2%)	10	Direct	21	30	36
		Correcting for NH_3 in sples.	23	32	36
Dried Skim Milk (32.8%)	6	Direct	29	33	35
		Correcting for NH_3 in sples.	34	35	39
Hard Boiled Egg (12.0%)	6	Direct	11	16	31
		Correcting for NH_3 in sples.	10	14	31
Expeller Processed Soy Meal (49.0%)	1	Direct	14	25	37
		Correcting for NH_3 in sples.	14	25	37

although the actual titration values are somewhat different, particularly in the case of the sunflower meal where appreciable amounts of amide nitrogen are found, the over-all picture of digestion of the protein remains the same.

Another point worthy of mention is the effectiveness of the antiseptic in the enzymic digestion mixture. Toluene has been employed for this purpose in the current studies. Tests conducted on whole beef blood, a favorable medium for the propagation of many types of bacteria, have indicated that toluene is very effective as a bacteriostatic and even as a bactericidal agent. The use of toluene and benzene in microbiological assays when test materials are incubated with enzymes for the liberation of the bound forms of vitamins is, of course, common practice. When ineffective bacteriostatic agents were employed, putrefaction occurred in the digestion mixtures, and the formol titration values were as much as 30 percent greater than the figures for the acid hydrolyzed samples. This was due to acid decomposition products which are also measured in the formol titration.

With all the factors mentioned under control, Table 7 presents data on the reproducibility of the technique for estimating the susceptibility of proteins to *in vitro* enzymic digestion. For each experiment 200 mg. of USP pancreatin of the same batch was employed. These duplicate series of enzymic digestions were carried out at different periods, some spaced as much as one month apart. The data show that the reproducibility of the test procedure is excellent. Insofar as the formol titration itself is concerned, the precision attainable is similar to that of the usual acidimetric-alkalimetric titrations.

TABLE 7

*Reproducibility of Technique for Estimating Susceptibility of Proteins to Enzymic Digestion**

Sample	Protein Content (N x 6.25)	Degree of Hydrolysis of the Proteins		
		After 1 Day	After 2 Days	After 5 Days
	percent	*percent*	*percent*	*percent*
Casein	91.6	18	30	41
		19	32	43
Solvent Processed Soy Flour	52.7	8	9	11
		8	12	14
Expeller Processed Soy Meal	46.2	13	23	31
		14	21	33
Defatted Sunflower Meal	51.4	12	26	38
		16	25	37
Whole Oats	14.3	19	26	30
		17	22	28

* For each experiment 200 mg. of USP pancreatin of the same batch was employed.

In vitro digestibility studies

The first application of the *in vitro* protein digestibility test was made to soybean products which had undergone heat-processing to improve their nutritive value. This type of material is well suited for studying the validity of the hypothesis that rate of digestibility is an important factor in determining the utilization of the amino acids, since it shows no difference in amino acid composition or coefficient of digestibility before and after various types of processing, but exhibits marked differences in biological value. The results of two series of digestibility studies are presented in Table 8.

TABLE 8

Susceptibility of Soy Proteins to Enzymic Digestion

Sample (Protein Content)	Laboratory Processing	Hydrolysis of Proteins		
		After 1 Day	After 2 Days	After 5 Days
		percent	*percent*	*percent*
Solvent Processed Soy Flour (52.7%)	None	8	9	11
	△ 100° C. 7 days, atmospheric pressure	8	9	11
	△ in water, 100° C. 5 min., atmospheric pressure	7	9	11
	Autoclaved 10 min. at 5 lbs. pressure	9	10	14
	Autoclaved 10 min. at 10 lbs. pressure	12	21	24
	Autoclaved 30 min. at 10 lbs. pressure	14	23	29
Expeller Processed Soy Grits (48.7%)	None	16	20	24
	Autoclaved 10 min. at 10 lbs. pressure	20	23	29
	Autoclaved 30 min. at 10 lbs. pressure	22	27	33
	Autoclaved 30 min. at 15 lbs. pressure	18	25	34
	Autoclaved 45 min. at 15 lbs. pressure	16	25	33

Dry heating of soy flour at 100° C. at atmospheric pressure results in no improvement in the biological value of the protein. The same is generally conceded if the material is heated for a short period of time in boiling aqueous suspension. However, heating with superheated steam or autoclaving results in an increase in the biological value of the protein *(34, 62, 63, 49, 25, 77)*. In this table are presented the results of tests of two soy products, one a solvent-processed soybean flour, the other an expeller-processed soy grit. The solvent processing of soy flour, extraction with a fat solvent at moderately low temperatures (in the neighborhood of 58° C.) is not very effective in increasing the biological value of the protein. On the other hand, the expeller process for obtaining fat from soybeans involves the building up of a high internal temperature in the pack so that the protein receives effective heat treatment at the same time the fat is being expelled. It will be noted from the data in Table 8 that those conditions which fail to affect the biological value of the soy protein also fail to increase the digestibility of the soy protein. Thus, the solvent-processed soy when heated at 100° C. either in the dry state or in aqueous suspension exhibits no improvement in rate and degree of digestibility of the protein component. As the material is autoclaved there is a progressive increase in its digestibility concomitant with the increase in biological value. In the case of the soy grits improved biological value is accompanied by greater degree and rate of digestibility of the untreated sample. Here, too, an increase in digestibility of the protein occurs as a result of the autoclaving. This soon plateaus out, hence there is no advantage in autoclaving beyond a limited period or at increased pressure. Inasmuch as the availability of certain of the amino acids may be reduced by excessive heat treatment, it may be found that at some point before maximum digestibility is obtained the product possesses maximum biological value. Almquist and collaborators *(2)* and Hayward and his group *(32)* have demonstrated that the limiting amino acid in soy protein is methionine and that autoclaving increases the availability of this amino acid. But precautions must be taken lest the effort to increase the availability of methionine be accompanied by decreased availability of other amino acids, notably lysine.

In Table 9 are listed the results obtained in studies of the influence of processing on the susceptibility of other proteins to *in vitro* enzymic digestion. The marked increase in the digestibility of the protein in whole egg after heat coagulation is in agreement with the reports in the literature *(3, 12, 31)*. The protein in whole beef blood shows a similar improvement in digestibility; in the case of the milk proteins the same is noted but to a lesser degree. Heating whole oats under steam pressure appears to be without effect on digestibility. Tests conducted on samples autoclaved for shorter and longer periods of time gave essentially the same results as the untreated samples. In the case of the defatted wheat germ there is a decrease both in degree and in rate of enzymic hydrolysis of the protein after the autoclaving treatment. The significance of these changes on the nutritive value of the proteins can be ascertained only by correlation with animal assays. In view of species differences in biological responses, recently noted *(13)* in protein utilization studies, precautions must be observed in drawing broad generalizations.

TABLE 9

Influence of Processing on the Susceptibility of Proteins to Enzymic Digestion

Sample	Processing	Hydrolysis of Proteins		
		After 1 Day	After 2 Days	After 5 Days
		percent	*percent*	*percent*
Whole Egg	Raw	1	8	12
	Hard Boiled	11	16	31
Milk	None	19	24	28
	Skimmed and spray dried	29	33	35
Whole Oats	None	19	26	30
	Autoclaved 30 min. at 15 lbs. pressure	17	22	27
Defatted Wheat Germ	None	29	38	52
	Autoclaved 30 min. at 15 lbs. pressure	16	29	38
Beef Blood	None	4	8	16
	Proteins heat coagulated	31	47	60

Biological and Microbiological Studies of Food Proteins Improved in Nutritive Value by Heat-Processing

The remainder of this paper is concerned with animal and microbiological assays designed to test the validity of the hypothesis dealing with the importance of the rate of digestibility of proteins *in vivo*. The soybean has been selected as the prototype of those proteinaceous products whose nutritional value is improved by heat-processing.

In Table 10 is a summary of the data obtained in correlating the *in vitro* tests of protein digestibility with rat growth studies. The soy products, the control milk sample, and the bioassay values were kindly supplied by Dr. J. W. Hayward of the Archer-Daniels-Midland Company. He has expressed the relative protein efficiency of the soy samples as the weight gained per gram of protein consumed, assuming an efficiency of 100 percent for milk proteins. It will be observed that the extracted and *toasted* soy meal was superior to the expeller soy meal, which in turn was superior to the raw soy meal. His studies also demonstrated that these differences in protein efficiency were not correlated with the coefficient of digestibility of the proteins. It will be noted that the *in vitro* digestibility tests of the

TABLE 10

Correlation of the In Vitro Test of Protein Digestibility With Rat Growth Studies

Sample*	*In Vitro* Hydrolysis of Proteins			Protein Efficiency In Rat Assay†
	After 1 Day	After 2 Days	After 5 Days	
	percent	*percent*	*percent*	*percent*
Dried Skim Milk	29	33	35	100
Extracted and Toasted Soy Meal	17	34	46	86
Expeller Soy Meal	13	23	31	71
Raw Soy Meal	12	19	26	53

* Samples and bioassay values kindly supplied by Dr. J. W. Hayward of Archer-Daniels-Midland Co., Mineapolis. The meals were from the same batch of soybean.

† As weight gained per gram of protein consumed, expressed relative to the milk protein having an assigned value of 100%.

soy meals show the very same relationship as the animal assays. However, comparisons should not be made with the results obtained with the dried skim milk since the amino acid composition of the protein in the latter is different from that of soy protein. The *in vitro* digestibility data should be compared only in respect to an individual protein material to ascertain the influence of processing or storage for extended periods of time.

In Table 11 is a correlation of the results of *in vitro* tests of soy protein digestibility with nitrogen balance studies on rats, using for the latter the procedure of Mitchell and associates *(53)*. No. 6 was the raw soy meal; No. 5 the solvent-extracted meal; the others were heat-processed. All the meals were prepared from the same batch of soybean. It will be noted, in considering the data obtained with meals No. 1 through 6, that the decrease in rate and degree of protein digestibility *in vitro* is accompanied by a decrease in the biological value, while the coefficient of digestibility of the protein is not significantly affected. In other words, the heat-processing fails to make available (absorbable) a greater amount of protein nitrogen for the rat to use in the building of new tissue protein. However, the percentage of absorbed nitrogen retained for tissue protein anabolism was much greater in the case of the processed soy No. 1 as compared with the raw meal No. 6.[†] It would seem that the protein in soy meal No. 1, by virtue of being much more readily digestible, liberates methionine (the limiting amino acid) at a more rapid rate and at a more opportune time in relation to the other amino acids which it supplements. In the case of the raw soy, the methionine may be liberated too late to supplement the amino acids already absorbed. Thus, not only is the methionine inefficiently utilized for protein synthesis, but other amino acids, which require methionine supplementation, are likewise poorly utilized, being converted to energy rather than tissue substance.

On the other hand, it might be assumed that the coefficient of digestibility, dropping from 84 to 81, would be of very great importance if the difference of 3 percent represented principally failure of methionine absorption. In that case, the differences in the biological values could be due simply to the degree rather than to the rate of methionine liberation *in vivo*. However, the hypothesis in the present study requires that the methionine in the raw soy be absorbed to almost the same extent as the methionine in the processed soy, but after too long a time interval effectively to supplement the other amino acids previously absorbed.

TABLE 11

Correlation of the In Vitro Test of Protein Digestibility With Nitrogen Balance Studies on the Rat: Studies With Soy Protein

Soy Meal*	*In Vitro* Hydrolysis of Proteins			Rat Assays of Proteins	
	After 1 Day	After 2 Days	After 5 Days	Biological Value	Coefficient of Digestibility
	percent	*percent*	*percent*	*percent*	*percent*
1	14	25	37	71	84
2	13	22	33	67	85
3	14	22	32	66	82
4	11	17	23	63	84
5	10	16	21	61	81
6	11	16	22	53	81
7	11	15	24	72	88

* Sample No. 6 was the raw soy meal; No. 5 the solvent extracted meal; the others were heat-processed. All the meals were prepared from the same batch of soybean.

Because of these conflicting interpretations, specific tests were designed to study the problem. These involved studies of methionine absorption by the rat consuming the test rations. In conducting the nitrogen balances according to the technique described by Mitchell *(53)*, it is necessary to feed the animals a low protein diet containing lactalbumin, at a level of about 3 to 4 percent of the ration, before and after the actual assays with the test proteins. In the course of these successive assay periods a dry skim milk sample is included, so that comparisons may be drawn between the biological value and coefficient of digestibility of the test samples with that of whole milk protein. The results of the methionine balance studies are summarized in Table 12.

It will be noted that despite an increased methionine intake of 250 percent by the feeding of the milk proteins, the same fecal excretion of this amino acid occurred.* This is good evidence that the 70 mg. of methionine

[†] The results with soy meal No. 7 are included in Table 13, although it is an exception to the general rule. The product was a heat-processed preparation, quite brown in color, with as high a biological value as soy meal No. 1, but it exhibited relatively poor digestibility *in vitro*. It may be that substances are present in this product as a result of the processing, inhibitory of enzymic activity *in vitro* but not *in vivo*.

TABLE 12

Methionine Absorption by the Rat Consuming Diets Containing Milk or Soy Protein

Ration*		Intake of Methionine	Fecal Excretion of Methionine	Unabsorbed Methionine		Assay of Proteins	
Description	Protein Content			Corrected‡	Part of Intake	Biological Value	Coefficient of Digestibility
	percent	*mg.*†	*mg.*†	*mg.*†	*percent*	*percent*	*percent*
Lactalbumin	2.96	61	65	0	0	....	....
Lactalbumin	2.96	65	69	0	0	....	....
Dried Skim Milk	8.50	225	75	0	0	89	84
Processed Soy—1	9.06	161	146	76	47	71	84
Processed Soy—2	9.09	178	150	80	45	67	85
Processed Soy—3	9.10	141	129	59	42	66	82
Processed Soy—4	9.24	200	147	77	38	64	84
Extracted Soy—5	9.30	158	133	63	40	61	81
Raw Soy—6	8.99	154	145	75	49	53	81

* The soy meals were all from the same batch of soybean.

† Per rat test period of 7 days.

‡ Correction is made for the metabolic fecal methionine, 70 mg. per rat per period. The same group of six adult rats was employed throughout the balance studies.

excreted per rat during the 7-day test period represented metabolic fecal methionine and not methionine derived from dietary protein. The processed, extracted, and raw soy meals were all fed at a protein level of approximately nine percent. Correction of the total fecal methionine for the metabolic excretion of methionine gives an index of the quantity of this amino acid which failed to be absorbed. Expressing this in terms of methionine intake, it was found that as much as 38 to 49 percent of the methionine in soy products was not absorbed from the gastrointestinal tract of the rat. Furthermore, this absorption of methionine showed no correlation with the biological value. The values for unabsorbed methionine were essentially the same considering the assumption of a constant metabolic excretion. The differences in biological value are significant since the values were reproducible within several percent. Johnson, Parsons, and Steenbock *(39)* have reported negligible decreases in fecal sulfur and nitrogen when raw soy meal was replaced with a properly cooked product. However, greater retention (decreased urinary excretions) of both these factors was noted when the heat-processed soy meal was fed. These observations are in complete harmony with the hypothesis presented in this report since they, too, indicate no decrease in methionine absorption when the raw soy is ingested, but poor utilization of both this and the other amino acids. More recently, Evans *(19)* reported no correlation between the "digestible" organic sulfur content of soy protein and its nutritional value.

The present experiment constitutes a specific case where degree of digestibility of the protein in the gastrointestinal tract as well as the extent of absorption of the limiting amino acid, methionine, are unchanged, but nevertheless, the biological value (retention of absorbed nitrogen) varies considerably. Apparently the methionine in the raw meal is absorbed so late during the gastrointestinal journey that this amino acid, as well as the incompletely supplemented amino acids, are not efficiently utilized for the synthesis of body protein.

The validity of this interpretation is supported by further experimental findings, presented in Table 13. The test materials were the raw soy and the processed meal with the highest biological value. The biological values and coefficients of digestibility of both products are listed. The percent of dietary methionine unabsorbed is also indicated. According to the *in vitro* test, one is more readily digested than the other. The proteins of both samples were then analyzed for three amino acids, leucine *(70, 48)*, lysine *(16)*, and methionine *(47, 1)*. The values are essentially the same for the two products and agree with those reported in the literature for soy protein. The digests obtained, in the course of the *in vitro* enzymic hydrolysis of the protein, at the end of the first and fifth days were also subjected to amino acid analysis. For this purpose trichloroacetic acid was added to the digest to make a 7 percent concentration. The filtrates were then heated to convert the trichloroacetic acid to chloroform and carbon dioxide which were volatilized from the boiling solutions. These were then subjected to acid hydrolysis to convert peptides and possibly larger molecules to the free amino acids. Thus the values for leucine, lysine, and methionine in the filtrates of the protein digests include not only these amino acids in the free state but also in peptide linkage not precipitable by 7 percent trichloroacetic acid. Obviously the percentage amino acids so liberated would be considerably greater than that estimated by formol titration which is a measure of only the free amino groups.

Methionine was liberated very slowly from raw soy as compared to leucine, while lysine was most rapidly released by enzymic digestion. In the case of the processed soy, the same relationship held, although all amino acids were released at a somewhat faster rate. When the five-day digests were tested, it was found that almost all the lysine and more than half of the leucine had been liberated. In the hydrolysate of the raw soy meal only 36 percent of the methionine was found, while in the digest of the heat-processed meal there was 73 percent. These data indicate that methionine is liberated from soy proteins at a slower rate than the other two amino acids, and that heat-processing of this protein increases the rate of liberation of the methionine to a much greater extent than of leucine or lysine.

Biological and Microbiological Studies of Food Proteins Impaired in Nutritive Value by Heat-Processing

Earlier in this report it was pointed out that excessive heat-processing reduces the biological value of protein without affecting materially the protein content, the essential amino acid composition, or the degree of protein digestibility *in vivo*. In such cases lysine has been found to be the principal limiting amino acid. These findings are comparable to those noted with raw foods, improved in protein value by heat-processing, with the

TABLE 13

Rate of Enzymic Liberation of Amino Acids During the In Vitro Test of Protein Digestibility As A Critical Factor in Determining Nutritional Response

Experiment	Raw Soy Meal (No. 6)	Processed Soy Meal (No. 1)
Rat Assays		
Biological Value of the Proteins, %	53	71
Coefficient of Digestibility of the Protein, %	81	84
Dietary Methionine Unabsorbed, %	49	47
In Vitro Enzymic Hydrolysis of Proteins*		
After 1 day, %	11	14
After 2 days, %	16	25
After 5 days, %	22	37
Amino Acid Composition of the Proteins†		
Leucine, %	7.1	7.7
Lysine, %	5.1	5.4
Methionine, %	2.2	2.2
Liberation of Amino Acids‡		
Leucine, %, After 1 Day Hydrolysis	28	33
Lysine, %, After 1 Day Hydrolysis	45	56
Methionine, %, After 1 Day Hydrolysis	5	10
Leucine, %, After 5 Days Hydrolysis	52	65
Lysine, %, After 5 Days Hydrolysis	77	84
Methionine, %, After 5 Days Hydrolysis	36	73

* Based upon liberation of free amino groups, as determined by formol titration.

† Analyses on acid hydrolyzed samples, values calculated to 16% nitrogen.

‡ Includes not only free amino acids but also peptides, liberated during the *in vitro* enzymic hydrolysis and not precipitated by 7% trichloroacetic acid. The values listed are percentages of the total.

exception that methionine is the limiting amino acid in the raw products. This portion of the report is concerned with an investigation designed to determine whether the same mechanism is responsible for the reduced biological value of excessively heat-processed protein; namely, impairment in the susceptibility of the protein to enzymic digestion with the result that the limiting amino acid is released *in vivo* too late to supplement the amino acids already absorbed.

The results of tests with two samples of dried skim milk are of interest and are present in Table 14. These samples were obtained from the same processor at two periods one year apart. The amino acid composition was, of course, the same, and yet when tested on rats the samples showed an appreciable difference in biological value, 78 percent as compared to 90 percent, but no significant difference in coefficient of digestibility, that is, the fraction of dietary protein absorbed from the gastrointestinal tract. However, the more readily digestible sample, according to the *in vitro* test, exhibited the higher biological value.

In subsequent studies designed specifically to determine what mechanism is responsible for the poor utilization of lysine in excessively heat-processed protein, casein was selected as the test material. In confirmation of the work of others *(5, 17)*, it has been found (see Table 15) that dry-heating the sample[5] at elevated temperature (150° C.) does not destroy the limiting amino acid, lysine. When the samples were subjected to maximal enzymic hydrolysis (peptic followed by pancreatic digestion), it may be noted (see Table 16) that the degree of protein hydrolysis was not affected by the heat treatment and that the microbiologically available lysine *(72)* content was not substantially reduced.

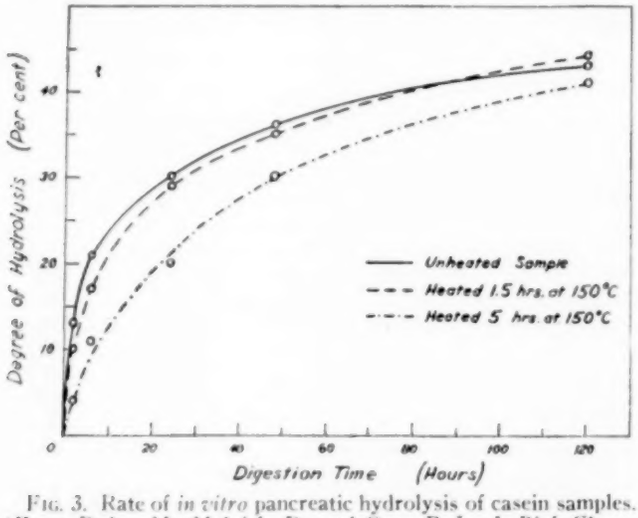


FIG. 3. Rate of *in vitro* pancreatic hydrolysis of casein samples. (From Pader, M., Melnick, D., and Oser, B. L. *J. Biol. Chem.*, 172, 763 [1948].)

In contrast to the above findings, striking differences in the *susceptibility* of the heated and unheated casein samples to *in vitro* pancreatic digestion are noted *(61)*. The data plotted in Figure 3 indicate that the heated protein samples are digested at significantly slower rates than the unheated control sample and that the rate of liberation of formol titratable nitrogen varies inversely with the processing time. The differences are of greatest relative magnitude during the early phase of hydrolysis. The ultimate degree of digestion of both the heated and unheated products eventually approaches the same value, in agreement with the results of the serial enzymic digestion experiments (see Table 16).

The differences in the *rate* of liberation of the available lysine from the casein samples are even more striking. Reference to Figure 4 shows that microbiologically available lysine was liberated from the heat-treated protein by pancreatin at a much slower rate than from the unheated product. The curves relating liberation of available lysine to time are linear up to a point at which they form a plateau. The relative slopes of the linear portions of the curves are as follows: 1, arbitrarily assigned to the control unheated sample; 0.66, casein heated 1.5 hours; and 0.25, sample heated 5 hours. Thus, substances with lysine activity are released from the unheated protein during the early period of digestion at a rate four times as great as from the sample submitted to prolonged heating, and 1.5 times as rapidly as from the intermediate preparation.

It is apparent that the differences in the content of microbiologically available lysine in the acid or final enzymic digests of heated and unheated casein are insufficient to account for the markedly reduced biological value of the heated protein. The results of the studies of

[5] The casein sample was obtained from the S. M. A. Corporation, Chagrin Falls, Ohio.

TABLE 14

Correlation of the In Vitro Test of Protein Digestibility With Nitrogen Balance Studies on the Rat: Studies With Milk Protein

Dried Skim Milk*	*In Vitro* Hydrolysis of Proteins			Rat Assays of the Proteins		
	After 1 Day	After 2 Days	After 5 Days	Series	Biological Value	Coefficient of Digestibility
	percent	*percent*	*percent*	*percent*	*percent*	*percent*
1	27	31	33	I	77	89
				II	79	87
2	32	36	41	I	90	85
				II	89	84

* Samples obtained from the same processor.

TABLE 15

The Lysine Content of the Test Casein Samples

Casein Sample	Lysine Found*
	percent
Unheated	8.1
Heated 1.5 hours at 150° C.	7.9
Heated 5 hours at 150° C.	7.6

* Determined microbiologically after complete acid hydrolysis; values calculated to the pure protein basis, 15.4 percent nitrogen.

TABLE 16

*Enzymic Liberation of Lysine for Microbiological Utilization**

Casein Sample	Degree of Hydrolysis**	Microbiologically Available Lysine†	Lysine Utilized‡
	percent	*percent*	*percent*
Unheated	57	6.5	80
Heated 1.5 hours at 150° C.	51	5.9	75
Heated 5 hours at 150° C.	57	5.2	68

* Peptic digestion followed by pancreatic digestion *(61)*.
** Estimated by formol titration.
† In the final enzymic digest, calculated to the original protein basis.
‡ Percent of total lysine in casein samples.

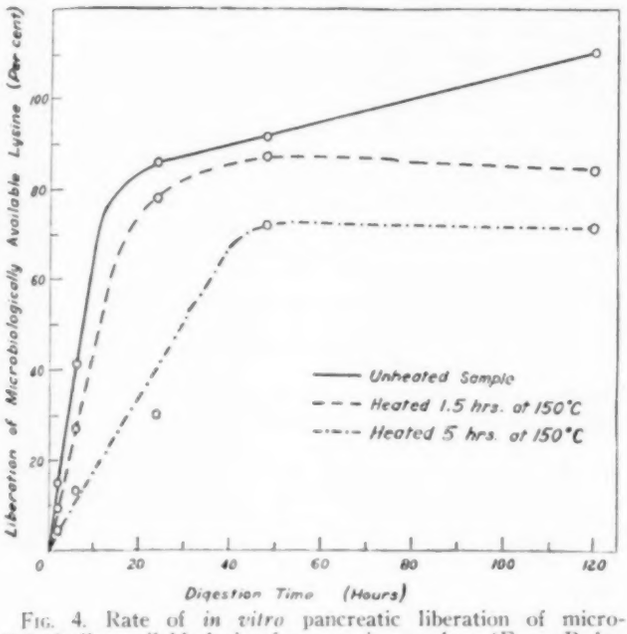


FIG. 4. Rate of *in vitro* pancreatic liberation of microbiologically available lysine from casein samples. (From Pader, M., Melnick, D., and Oser, B. L. *J. Biol. Chem.*, **172**, 763 [1948].)

the rate of liberation of lysine for microbiological utilization provide a plausible explanation for the impairment of the biological value. The rate of release (and absorption) of lysine from heat-processed casein is too slow to permit effective supplementation of the other essential amino acids *in vivo* with the result that nitrogen retention for tissue protein synthesis is impaired; hence the need for supplementing the heated casein with lysine for optimal utilization. Indeed, from the work of others *(64)* the lysine in excessively heat-processed protein may be released so late during the gastrointestinal journey that a large fraction may escape absorption.

Biological Studies of Food Proteins Whose Nutritive Value Is Not Affected by the Heat-Processing Employed

The proteins in excessively heat-processed cereals are recognized to exhibit little nutritive value *(56, 44, 58, 71, 43, 64)*. However, when these are properly cooked no undesirable changes in the protein component occur. In fact the protein in the unheated products appear to be equal in nutritive value to those cooked for improved palatability *(65)*.

In studies, summarized in Table 17, of various oat samples(raw, pan-toasted, and thoroughly cooked at atmospheric pressure), no significant differences in the digestibility of the protein *in vitro* were noted. All four products were rapidly hydrolyzed and reached a maximum degree of digestibility according to this type of test. The lack of effect of the heat-processing on the digestibility of oat protein is also evidenced by the uniformity in its biological value as determined by the nitrogen balance experiments. The somewhat greater value of 81 percent for the whole oats may be attributed in part to a difference in the quality of the protein consumed since the protein in this sample comes from the bran as well as the endosperm.

TABLE 17

Correlation of the In Vitro Test of Protein Digestibility With Nitrogen Balance Studies on the Rat: Studies With Oat Protein

Oat Sample*	*In Vitro* Hydrolysis of Proteins			Rat Assays of Proteins	
	After 1 Day	After 2 Days	After 5 Days	Biological Value	Coefficient of Digestibility
	percent	*percent*	*percent*	*percent*	*percent*
Whole Oats	27	40	51	81	85
Hulled and "Pan Toasted"	25	34	44	74	87
Cooked	18	36	53	75	88
Cooked	20	40	47	79	89

* From the same batch of oats.

Summary and Conclusions

The concept of food protein as N × 6.25 should be extended to include a consideration of both the functional and nutritive properties of the protein. The functional properties, readily modified by heat-processing, affect appearance and palatability of the end-product and for this reason cannot be dissociated from the nutritive properties of the protein. The functional properties of the protein are usually evaluated by subjective utility tests; it has been suggested that these be supplemented with precise objective procedures for determining the degree of protein denaturation caused by the heat-processing.

The nutritive properties of protein may be determined by animal assays but here also the need to supplement the data with results of *in vitro* tests has been emphasized. Determinations of the essential amino acid composition of the protein and its susceptibility to enzymic digestion contribute to an explanation of results obtained by animal assays. A simple *in vitro* procedure for determining the susceptibility of protein to enzymic digestion has been presented in this report. It has been shown in studies with products, improved or impaired by heat-processing and exhibiting no change in amino acid composition or degree of digestibility, that rate of enzymic digestion is critical. For optimal utilization of food proteins all essential amino acids must not only be available for absorption but must be liberated during digestion *in vivo* at rates permitting mutual supplementation.

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The Effect of Acid Foods on Aluminum Cooking Utensils[a]

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The effects of acid foods on aluminum cooking utensils have been determined. Rhubarb and cherry juices dissolve the most aluminum from the utensils. The juices have less effect on wrought aluminum utensils than on cast aluminum utensils. Acidity is an important factor in the action of acid juices on aluminum utensils.

Introduction

A previous publication *(13)* presents the effects of dilute acids, which are usually present in fruits and vegetables, on strips of aluminum and on aluminum cooking utensils. Of the 0.1 normal organic acids used, trichloroacetic, acetic, formic, monochloroacetic, and lactic were the most active, in the order named, when the solutions of acids were boiled 30 minutes daily in contact with the aluminum. Oxalic acid, in normal solution, was very active at a temperature of 25° C. The present communication records the corrosive effect of fruit juices on various brands of commercial aluminum cooking utensils.

Many investigations have been made on the toxicity of aluminum added to food products. The general conclusion has been that small amounts have no detrimental effect in the body. These conclusions are confirmed in leading books on toxicology *(6, 9, 16)*. The Referee Board appointed by President Theodore Roosevelt in 1907 *(15)* reports that aluminum in baking powder, furnishing a daily intake up to 150 mg. of aluminum, contributed no poisonous or other deleterious effects which might be injurious to health.

The effects of acid foods on aluminum utensils have received some attention. Glaister and Allison *(8)* report that the amounts of aluminum dissolved by orange,

[a] Presented at the Detroit meeting, A. C. S. September, 1940.

lemon, and tomato products are extremely small. Blough *(3)* comes to the same conclusion when tomato products are cooked in aluminum. Blount and Bailey *(4)*, Rohrig *(14)*, and Mrak and Cruess *(11)*, all conclude that juices of citrus fruits have rather great effects on aluminum. Colobraro *(5)* states that tomato products dissolve considerable amounts from aluminum utensils. Beal, Unangst, Wigman, and Cox *(1)*, and Fillinger *(7)* report that acid foods dissolve very small amounts of aluminum.

Procedure and Methods

Twelve different brands of aluminum cooking utensils were used in this research. Of these, five were made from cast aluminum and seven were made from wrought aluminum. These utensils, representing standard brands of aluminum cooking pans, were purchased on the open market. Aluminum used to make cooking utensils usually contains from 97 to 99 percent aluminum. The percentages of such elements as copper, silicon, magnesium, iron, and zinc sometimes are present in a few tenths percent each. Manganese may be present in amounts up to 1.0 percent.[b]

Cherry, orange, tomato, and rhubarb juices were prepared from the fresh fruits. The cherries were washed, the stems removed, and the fruit was boiled in a covered porcelain dish. The juice was extracted by means of a small hand juice-extractor, and was then strained through cotton. The oranges were reamed by hand, and the juice was strained before it was used. The tomatoes were cut into small wedge-shaped pieces and cooked in a covered porcelain dish. The juice and pulp were passed through a fine rotary sieve to separate them from the skin and seeds. The rhubarb was cut into small pieces, cooked in a porcelain dish with a small amount of water, and pressed. The added water was evaporated during the cooking process.

The sweetened canned fruit juices used were pear, plum, peach, loganberry, grapefruit, orange, pineapple, apricot, and prune. The unsweetened canned juices used were orange, grapefruit, pineapple, grape, apple, and yellow tomato.

Into each of the aluminum pans was placed a measured amount of a given juice. The contents of each container were heated directly over a flame to the boiling point, and then allowed to simmer on the steam bath for 30 minutes. After the heating process was completed, the volume was adjusted to the original amount with distilled water. Fifty-ml. amounts of each juice were measured into platinum dishes, evaporated to dryness, charred and ashed in the muffle furnace at a temperature not to exceed 650° C. A blank was run on each sample of juice in order to determine the amount of aluminum in the original juice. A single sample of juice was used for the tests in each of the different utensils. After cooking the juice in a given utensil, the pan was cleaned with fine steel wool.

The method used for the determination of aluminum was the official method for iron and aluminum in plant material as given by the Association of Official Agricultural Chemists *(12)*. Duplicate determinations were made in every instance.

The increased amounts of aluminum found in the juices, after being cooked in aluminum utensils, were calculated to parts per million. The results obtained, when wrought aluminum utensils were employed, are given in Table 1. Table 2 records the results in parts per million of aluminum dissolved by fruit juices in cast aluminum utensils. Table 3 records the relative acidities of the fruit juices used.

The results given in Table 1 show that rhubarb, cherry, prune, loganberry, and yellow tomato juices dissolved the most aluminum from the wrought aluminum utensils. Pear, apricot, peach, and pineapple juices proved to be the least effective on these utensils. All of these latter juices contained added sugar. Utensils numbers 6 and 8 were most affected by the different juices, and number 2 the least affected. According to the retailer, pans numbers 1 and 3 were of the same wrought aluminum composition, but sold under different trade names. The amounts of aluminum dis-

[b] Personal communication, Aluminum Company of America.

TABLE 1

Parts Per Million of Aluminum Dissolved By Fruit Juices in Wrought Aluminum Utensils

Fruit Juice	Amt. in Original Juice	1†	2	3	4	5	6	7	8	Average increase in aluminum
Apple	2.2	16.0	19.6	29.3	18.0	20.7	17.0	26.3	26.6	21.7
*Apricot	1.8	3.3	3.7	5.3	5.7	9.2	16.5	15.2	12.5	8.9
Cherry (fresh)	5.3	60.3	51.8	69.3	71.5	61.0	96.3	68.0	88.9	70.9
Grape	3.1	10.3	7.7	10.7	11.3	14.7	26.0	10.7	8.3	12.5
*Grapefruit	4.0	17.6	15.3	17.6	16.0	25.3	36.0	14.3	24.0	20.8
Grapefruit	4.4	8.3	14.7	12.0	15.0	18.3	18.3	16.3	31.6	16.8
*Loganberry	4.4	18.6	20.3	22.0	32.0	52.3	83.0	39.0	60.8	41.0
Orange (fresh)	1.3	4.9	4.4	6.7	10.2	18.0	18.3	12.7	24.0	12.4
*Orange	4.0	7.3	8.3	13.0	11.1	15.7	25.0	15.6	24.5	15.1
Orange	4.3	16.0	10.3	17.6	14.0	20.7	20.3	15.7	16.7	16.4
*Peach	2.0	13.3	11.3	12.0	11.7	11.3	10.7	9.3	10.6	11.3
*Pear	2.0	8.3	10.3	10.3	8.7	6.3	7.7	6.3	5.3	7.9
*Plum	2.7	11.3	10.7	14.7	17.6	15.3	18.7	16.3	25.4	16.3
*Pineapple	4.0	9.7	4.0	9.7	10.7	11.0	18.0	16.3	12.7	11.5
Pineapple	3.6	14.0	13.7	16.0	24.0	26.0	37.6	20.3	29.8	22.7
*Prune	6.2	27.0	33.0	49.0	44.6	36.3	51.9	36.6	54.0	41.6
Rhubarb (fresh)	23.5	102.6	92.3	166.8	197.5	180.5	209.9	200.9	169.6	165.0
Tomato (fresh)	3.1	9.3	10.0	13.0	11.0	20.3	18.6	12.3	16.5	13.9
Yellow Tomato	3.1	21.0	14.0	13.7	31.3	40.0	38.3	55.0	54.0	33.4
Average amount aluminum dissolved from each pan		20.0	18.7	26.8	29.6	31.7	40.4	32.0	36.6	

* Contained added sugar.

† Numbers indicate the different brands of aluminum utensils used.

solved from these two utensils, however, differed considerably.

In the investigation *(13)* in this laboratory on the effect of organic acids on aluminum, it was found that a normal solution of oxalic acid had a decided corrosive action on sheet aluminum. The great corrosive effect of rhubarb noted in the present investigation may be because of the presence of oxalic acid in this food product.

As a rule the presence of sugar in a juice causes less aluminum to be dissolved. This condition was reported by Beal, Unangst, Wigman, and Cox *(1)*. Too much emphasis should not be placed on this observation from the results herein reported, because in all instances, except one, the sweetened and unsweetened juices were from different sources. Ten percent sugar was added to the unsweetened pineapple juice; therefore, with this juice the protective effect of sugar seems to be indicated. Contrary to the usual results, unsweetened grapefruit juice did not remove as much aluminum from the utensil as the sweetened product.

Fresh orange juice dissolved less aluminum than the sweetened canned juice, and the latter juice dissolved less than the unsweetened canned juice. The last two juices, however, were not from the same source, so a comparison between them, perhaps, is not justified. Yellow tomato juice removed larger amounts of aluminum from the utensils than the fresh red tomato juice.

In the cast aluminum utensils (Table 2), as with wrought utensils, rhubarb and cherry juices dissolved the most aluminum; yellow tomato, pineapple, and sweetened orange juices were next in order. Unsweetened grapefruit and pineapple juices both dissolved more aluminum than the sweetened juices of the same fruits. Peach, grape, pear, and apricot juices had less effect on cast aluminum utensils than other juices.

On the average, cast aluminum utensils 2 and 3 were most affected by the fruit juices and utensil 5 was the least affected. On an average with each of the juices, except prune juice, the cast aluminum utensils showed more parts per million of aluminum dissolved than did the wrought aluminum utensils.

Referring to Table 3, it may be seen that the most acid juices are rhubarb, grapefruit, and cherry. The least acid juices are pear and peach. The most acid juice, rhubarb, dissolved the greatest amount of aluminum from the pans; and the least acid juices, pear and peach, dissolved a very small amount of aluminum. The next most acid juice, unsweetened grapefruit, dissolved very little aluminum, occupying tenth place with wrought aluminum utensils and twelfth place with cast aluminum utensils in the amount of aluminum dissolved. Acidity, therefore, is an important factor, but not necessarily the controlling factor, in the action of acid juices on aluminum utensils.

TABLE 2

Parts Per Million of Aluminum Dissolved By Fruit Juices in Cast Aluminum Utensils

Fruit Juice	1†	2	3	4	5	Average increase in aluminum
Apple	33.5	57.3	74.1	37.7	19.8	44.5
*Apricot	22.2	23.8	34.2	26.6	20.3	25.4
Cherry (fresh)	143.7	167.7	208.2	103.8	100.2	144.7
Grape	16.3	26.0	18.6	17.5	9.3	17.5
*Grapefruit	26.0	27.8	33.7	30.2	31.6	29.9
Grapefruit	30.4	28.9	38.7	40.4	26.6	33.0
*Loganberry	32.9	59.4	47.4	30.9	58.3	45.8
Orange (fresh)	34.2	57.0	44.7	35.7	65.3	47.4
*Orange	57.1	64.1	57.1	57.7	38.0	54.8
Orange	31.3	22.1	25.2	20.9	44.3	28.8
*Peach	26.4	16.4	11.9	20.0	6.7	16.3
*Pear	24.2	27.2	20.1	26.6	7.7	21.2
*Plum	34.0	34.6	22.2	36.9	29.6	31.5
*Pineapple	34.0	32.6	75.5	49.5	36.0	45.5
Pineapple	64.8	38.4	58.6	85.2	47.6	58.9
*Prune	28.6	70.2	37.3	29.5	23.6	37.8
Rhubarb (fresh)	337.3	336.9	510.6	250.0	262.8	339.5
Tomato (fresh)	35.5	54.6	60.8	36.0	46.0	46.6
Yellow Tomato	67.5	68.8	132.3	103.7	52.0	84.9
Average amount of aluminum dissolved from each pan	56.8	63.9	79.5	54.7	48.7	

* Contained added sugar.
† Numbers indicate the different brands of aluminum utensils used.

TABLE 3

Acidity of Fruit Juices

Fruit Juice	ml. N/10 NaOH to neutralize the acid in 100 ml. juice	Grams acid per 100 ml. of juice as malic acid
Apple	113.3	0.76
*Apricot	61.8	0.41
Cherry (fresh)	164.8	1.10
Grape	92.1	0.62
*Grapefruit	185.4	1.24
Grapefruit	195.7	1.31
*Loganberry	133.9	0.90
Orange (fresh)	154.5	1.04
*Orange	133.9	0.90
Orange	123.6	0.89
*Peach	39.0	0.26
*Pear	20.6	0.14
*Plum	92.1	0.62
*Pineapple	154.5	1.04
Pineapple	154.5	1.04
*Prune	51.5	0.35
Rhubarb (fresh)	236.9	1.59
Tomato (fresh)	82.4	0.55
Yellow Tomato	92.7	0.62

* Contained added sugar.

The blank determinations show much more aluminum present in rhubarb than in any of the other foods tested. Prune and cherry juice were next in aluminum content. The amount of aluminum present in the blanks, except with the fresh fruit juices, may be partly due to the preparations of the fruit for canning in aluminum utensils and also to the storage of the juice in tin cans.

Table 4 shows the aluminum content of fresh foods as reported by other investigators *(10)*. The results are expressed as mg. per 100 g. of dried food. Some of the determinations recorded in this table were made as early as 1904, and others date to 1932. There is considerable difference among some of the results. For instance, Berg reports 0.33 mg. of aluminum in apples; whereas Massatsch reports 1.9 mg.; Lehman reports 0.28 mg. of aluminum in oranges; whereas Winter and Bird report 0.94 mg. No doubt these differences were due partly to the methods of analysis used, and the nature of the soils in which the foods were grown. The early methods for the determination of aluminum in food were not so accurate as some of the methods later developed. Beal, Unangst, Wigman, and Cox *(1)* and Bertrand and Levy *(2)* are two of the most recent reports on the analysis of a large number of foods for aluminum.

From Tables 1 and 2 it may be seen that the amounts

TABLE 4

*Results of Other Investigators**
(Figures are given in mg. per 100 g. dried substance)

Fruit	Langworthy, and Austen, 1904	Ragnar Berg, 1913	Underhill and Peterman, 1929	Massatsch, 1929	Winter and Bird, 1929	Lehman, 1929-1931	Bertrand and Levy, 1931
Apples	1.3	0.33	0.1-0.53	1.9	0.84	1.8	1.3
Apricots	.....	.....	.....	.....	.....	.....	6.0
Cherries	.....	.....	.....	.....	.....	.....	7.1
Grapefruit	.....	.....	.....	.....	0.75	.....	.....
Oranges	0.45	0.35	0.51	.....	0.94	0.28	0.6
Peaches	.....	.....	.....	.....	.....	.....	6.4
Prunes	.....	.....	.....	.....	2.05	.....	.....
Rhubarb	.....	.....	.....	.....	6.33	.....	3.2
Tomatoes	.....	.....	.....	2.8	.....	3.8	2.2

* Taken from "A select, annotated bibliography on the hygienic aspects of aluminum and aluminum utensils." Mellon Institute of Industrial Research, Bibliographic Series, Bulletin No. 3, Pittsburgh, Pa. (1933).

of aluminum dissolved by foods were very small and below the amounts found by most investigators to have any physiological effect on the body.

Conclusions

1. Fruit juices have less effect on wrought aluminum utensils than on cast aluminum utensils.
2. For the most part, unsweetened juices tend to dissolve more aluminum than sweetened juices.
3. All of the original fruit juices tested contain some aluminum.
4. There is no regularity of action of a given juice on the different brands of aluminum utensils.
5. Rhubarb and cherry juice have a greater effect on both wrought and cast aluminum vessels than any of the other juices tested.
6. The degree of acidity of the juice may be responsible to some extent for the amount of action on aluminum, as shown by rhubarb and cherry juices.
7. The amounts of aluminum dissolved from the different brands of aluminum utensils are small. According to most investigators, such amounts are below those which have any physiological effects on the body.

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MEETING, AMERICAN SOCIETY OF BREWING CHEMISTS

On behalf of the Executive Committee of the American Society of Brewing Chemists, President Philip P. Gray has announced that the next Annual Meeting of the ASBC will be held at New Orleans, Louisiana, April 10 to 14, 1949, with headquarters at the Roosevelt Hotel. The choice of New Orleans is in line with the Society's policy to rotate the annual conventions geographically. At the same time, it is also a recognition of the importance of the brewing industry of the South and its growing membership in the ASBC.

Interesting and diversified activities are being planned for the New Orleans meeting. Under the leadership of Robert I. Tenney, Chairman of the Technical Committee, reports will be given on the progress of the various technical projects. Dr. Eric Kneen has accepted the chairmanship of the Program Committee and the presentation of individual research papers of high caliber is assured. Local arrangements are being made by a committee headed by Ulysses C. Gramsch. Further details will be announced.

VEGETABLE AND FRUIT PROCESSORS' SCHOOL

The Division of Horticultural Products of the Department of Horticulture, The Ohio State University, Columbus, Ohio, has announced the program for the second Vegetable and Fruit Processors' School which will be held at the Horticulture and Forestry Building in Columbus, March 14-16, 1949.

Nine lectures will deal with the subject of food preservation, there will be laboratory exercises covering processing technics and the examination of horticultural products, and there will be periods of discussion in which a wide variety of subjects will be covered.

Food Wastage — A Technology Problem

The problem of food supply is one that involves production and utilization. It should be understood that our food standard is one of the highest in the world and every move should emphasize the need to raise the level in those foods that furnish satisfaction and good nutrition. The problem of food supply is not one that is immeditely pressing in this country. Better processing, preservation, and distribution to prevent loss of nutrients as well as actual loss of food is of equal importance to increased production in keeping a balance between food supply and increased population.

The time will come when our present rate of food wastage due to spoilage in the field, in storage and distribution channels, and in the kitchen cannot be tolerated even in our own country without lowering our standards seriously. What percentage of our supply is wasted is unknown. It is sufficiently large however to offer ample reward for technological developments that will improve conservation. Such conservation may be effected in many ways that are not ordinarily classed as preservation. More convenient packaging should discourage waste in the home. Better storage and better processing may avoid waste of nutrients through deterioration. New developments in harvesting methods will certainly avoid large field losses. These savings are of equal importance with increased production in our race to feed a rapidly growing population.

The world has been slow in solving its food problems, but, for that matter, it has been slow in solving its transportation, communication, clothing, and housing problems. The difference is that people have always recognized food shortage while they had no conception of airplanes, telephones, nylon, and insulated houses, until these things were developed and handed to them. Therefore, one might have expected more attention to the food situation at an earlier date. The plain fact is that developments in all of these fields could not possibly have taken place until man had perfected the experimental method of acquiring accurate information about himself and his environment.

If developments in food have appeared to be somewhat less spectacular than in electronics, let us remember that the human body which utilizes this food is a most intricate system of balanced and coordinated chemical reactions with a fixed relationship. Since we cannot change the machine which uses the food, we must always have products that possess the nutrients in a form not greatly different than that eaten by our ancestors a hundred thousand years ago. While we know much more about the source, the chemical composition, and the function of these nutrients, we have not been able to make any important substitutions. Except for a few of the vitamins which have been synthesized, it may be said that we are dependent today on the same natural sources for our food as were our earliest predecessors. The boundaries that circumscribe the efforts of food scientists are likely to remain until some millions of years may allow the evolution of man into a different physiological specimen.

While the limitation may thwart the ambitious promoter who would like to be the first to provide the astonished world with a square meal in a package no larger than an aspirin tablet, it should also serve as an important guide to the more practical food technologist. Our field is now clearly marked as production, processing, preservation, packaging and distribution of the many long recognized food items in such a manner as to provide the consumer with enough of all the nutrients in palatable form, convenient to use and free of contamination. Meeting these requirements for a world population under the widest possible variation of environment and with each variant under continuous change, but with each consumer a rigidly fixed physiological unit, should be sufficient challenge. These are the problems of the food techcnologist.

R. C. Newton
I. F. T. President 1942-43

New or Old White House?

Since President Truman, in his inaugural address, expressed the idea that "We must embark upon a bold new program of making the benefits of our scientific advances and industrial progress available for the improvement and growth of underdeveloped areas," there has been much discussion of two questions; first, to what extent are we qualified to benefit the underdeveloped areas by transmitting to them knowledge of our scientific advances and industrial progress? second, what accounts for the fact that we are able to show the way technologically to other nations, if we are so qualified?

Many comparisons are being made. A favorite of these involves Great Britain and the United States, although, in such a comparison, we neglect the "underdeveloped areas." In this comparison, we learn that, for research, Britain spends 0.9 percent of its national income, and United States spends 0.6 percent of its national income. These expenditures amount to $6.75 per capita in the United Kingdom and $7.95 per capita in the United States. Since $6.75 will pay for more research in Great Britain than will $7.95 in the United States, it appears that research is at least more intense in Great Britain than in the United States. One may state that results seem to reflect the logical expectation from that situation—that Great Britain leads the United States in the production of fundamental scientific knowledge.

In admitting this fact, we have not answered the question of to what extent the United States is qualified to help other nations technologically. Certainly, if the United States is qualified to help Great Britain, one of the world's most advanced nations, it is more than qualified to help a "backward" nation, as Mr. Truman suggests. To answer the question, we may simply say that it is generally admitted that technology in the United States is ahead of technology in any other country. That seems to be a fairly satisfactory answer to question No. 1.